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# Lanthanide and Actinide Chemistry

**Simon Cotton**

*Uppingham School, Uppingham, Rutland, UK*



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In memory of Ray and Derek Cotton, my parents.

*Remember that it was of your parents you were born;  
how can you repay what they have given to you?*

*(Ecclesiasticus 7.28 RSV)*

also in memory of María de los Ángeles Santiago Hernández,  
a lovely lady and devout Catholic, who died far too young.

and to Lisa.





Dr Simon Cotton obtained his PhD at Imperial College London. After postdoctoral research and teaching appointments at Queen Mary College, London, and the University of East Anglia, he has taught chemistry in several different schools, and has been at Uppingham School since 1996. From 1984 until 1997, he was Editor of Lanthanide and Actinide Compounds for the *Dictionary of Organometallic Compounds* and the *Dictionary of Inorganic Compounds*. He authored the account of Lanthanide Coordination Chemistry for the 2nd edition of *Comprehensive Coordination Chemistry* (Pergamon) as well as the accounts of Lanthanide Inorganic and Coordination Chemistry for both the 1st and 2nd editions of the *Encyclopedia of Inorganic Chemistry* (Wiley).

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# Contents

<b>Preface</b> . . . . .	xv
<b>1 Introduction to the Lanthanides</b> . . . . .	1
1.1 Introduction . . . . .	1
1.2 Characteristics of the Lanthanides . . . . .	2
1.3 The Occurrence and Abundance of the Lanthanides . . . . .	2
1.4 Lanthanide Ores . . . . .	3
1.5 Extracting and Separating the Lanthanides . . . . .	3
1.5.1 Extraction . . . . .	3
1.5.2 Separating the Lanthanides . . . . .	4
1.6 The Position of the Lanthanides in the Periodic Table . . . . .	6
1.7 The Lanthanide Contraction . . . . .	7
<b>2 The Lanthanides – Principles and Energetics</b> . . . . .	9
2.1 Electron Configurations of the Lanthanides and f Orbitals . . . . .	9
2.2 What do f Orbitals Look Like? . . . . .	10
2.3 How f Orbitals affect Properties of the Lanthanides . . . . .	10
2.4 The Lanthanide Contraction . . . . .	11
2.5 Electron Configurations of the Lanthanide Elements and of Common Ions . . . . .	12
2.6 Patterns in Ionization Energies . . . . .	12
2.7 Atomic and Ionic Radii . . . . .	14
2.8 Patterns in Hydration Energies (Enthalpies) for the Lanthanide Ions . . . . .	14
2.9 Enthalpy Changes for the Formation of Simple Lanthanide Compounds . . . . .	14
2.9.1 Stability of Tetrahalides . . . . .	14
2.9.2 Stability of Dihalides . . . . .	17
2.9.3 Stability of Aqua Ions . . . . .	18
2.10 Patterns in Redox Potentials . . . . .	19
<b>3 The Lanthanide Elements and Simple Binary Compounds</b> . . . . .	23
3.1 Introduction . . . . .	23
3.2 The Elements . . . . .	23
3.2.1 Properties . . . . .	23
3.2.2 Synthesis . . . . .	24
3.2.3 Alloys and Uses of the Metals . . . . .	25
3.3 Binary Compounds . . . . .	25
3.3.1 Trihalides . . . . .	25
3.3.2 Tetrahalides . . . . .	27
3.3.3 Dihalides . . . . .	28
3.3.4 Oxides . . . . .	29

3.4	Borides . . . . .	31
3.5	Carbides . . . . .	31
3.6	Nitrides . . . . .	31
3.7	Hydrides . . . . .	31
3.8	Sulfides . . . . .	32
<b>4</b>	<b>Coordination Chemistry of the Lanthanides . . . . .</b>	<b>35</b>
4.1	Introduction . . . . .	35
4.2	Stability of Complexes . . . . .	35
4.3	Complexes . . . . .	37
4.3.1	The Aqua Ions . . . . .	37
4.3.2	Hydrated Salts . . . . .	37
4.3.3	Other O-Donors . . . . .	38
4.3.4	Complexes of $\beta$ -Diketonates . . . . .	39
4.3.5	Lewis Base Adducts of $\beta$ -Diketonate Complexes . . . . .	41
4.3.6	Nitrate Complexes . . . . .	41
4.3.7	Crown Ether Complexes . . . . .	41
4.3.8	Complexes of EDTA and Related Ligands . . . . .	42
4.3.9	Complexes of N-Donors . . . . .	43
4.3.10	Complexes of Porphyrins and Related Systems . . . . .	44
4.3.11	Halide Complexes . . . . .	46
4.3.12	Complexes of S-Donors . . . . .	46
4.4	Alkoxides, Alkylamides and Related Substances . . . . .	47
4.4.1	Alkylamides . . . . .	47
4.4.2	Alkoxides . . . . .	48
4.4.3	Thiolates . . . . .	50
4.5	Coordination Numbers in Lanthanide Complexes . . . . .	50
4.5.1	General Principles . . . . .	50
4.5.2	Examples of the Coordination Numbers . . . . .	51
4.5.3	The Lanthanide Contraction and Coordination Numbers . . . . .	53
4.5.4	Formulae and Coordination Numbers . . . . .	54
4.6	The Coordination Chemistry of the +2 and +4 States . . . . .	54
4.6.1	The (+2) State . . . . .	55
4.6.2	The (+4) State . . . . .	56
<b>5</b>	<b>Electronic and Magnetic Properties of the Lanthanides . . . . .</b>	<b>61</b>
5.1	Magnetic and Spectroscopic Properties of the $\text{Ln}^{3+}$ Ions . . . . .	61
5.2	Magnetic Properties of the $\text{Ln}^{3+}$ Ions . . . . .	62
5.2.1	Adiabatic Demagnetization . . . . .	65
5.3	Energy Level Diagrams for the Lanthanide Ions, and their Electronic Spectra . . . . .	65
5.3.1	Electronic Spectra . . . . .	66
5.3.2	Hypersensitive Transitions . . . . .	68
5.4	Luminescence Spectra . . . . .	69
5.4.1	Quenching . . . . .	73
5.4.2	Antenna Effects . . . . .	73
5.4.3	Applications of Luminescence to Sensory Probes . . . . .	74
5.4.4	Fluorescence and TV . . . . .	75
5.4.5	Lighting Applications . . . . .	76

5.4.6	Lasers . . . . .	76
5.4.7	Euro Banknotes . . . . .	77
5.5	NMR Applications . . . . .	77
5.5.1	$\beta$ -Diketonates as NMR Shift Reagents . . . . .	77
5.5.2	Magnetic Resonance Imaging (MRI) . . . . .	78
5.5.3	What Makes a Good MRI Agent? . . . . .	79
5.5.4	Texaphyrins . . . . .	81
5.6	Electron Paramagnetic Resonance Spectroscopy . . . . .	82
5.7	Lanthanides as Probes in Biological Systems . . . . .	83
<b>6</b>	<b>Organometallic Chemistry of the Lanthanides . . . . .</b>	<b>89</b>
6.1	Introduction . . . . .	89
6.2	The +3 Oxidation State . . . . .	89
6.2.1	Alkyls . . . . .	89
6.2.2	Aryls . . . . .	90
6.3	Cyclopentadienyls . . . . .	91
6.3.1	Compounds of the Unsubstituted Cyclopentadienyl Ligand ( $C_5H_5 = Cp$ ; $C_5Me_5 = Cp^*$ ) . . . . .	91
6.3.2	Compounds $[LnCp^*_3]$ ( $Cp^* =$ Pentamethylcyclopentadienyl) . . . . .	94
6.3.3	Bis(cyclopentadienyl) Alkyls and Aryls $LnCp_2R$ . . . . .	95
6.3.4	Bis(pentamethylcyclopentadienyl) Alkyls . . . . .	96
6.3.5	Hydride Complexes . . . . .	98
6.4	Cyclooctatetraene Dianion Complexes . . . . .	98
6.5	The +2 State . . . . .	99
6.5.1	Alkyls and Aryls . . . . .	99
6.5.2	Cyclopentadienyls . . . . .	100
6.5.3	Other Compounds . . . . .	100
6.6	The +4 State . . . . .	101
6.7	Metal–Arene Complexes . . . . .	101
6.8	Carbonyls . . . . .	102
<b>7</b>	<b>The Misfits: Scandium, Yttrium, and Promethium . . . . .</b>	<b>107</b>
7.1	Introduction . . . . .	107
7.2	Scandium . . . . .	107
7.2.1	Binary Compounds of Scandium . . . . .	108
7.3	Coordination Compounds of Scandium . . . . .	108
7.3.1	The Aqua Ion and Hydrated Salts . . . . .	108
7.3.2	Other Complexes . . . . .	109
7.3.3	Alkoxides and Alkylamides . . . . .	111
7.3.4	Patterns in Coordination Number . . . . .	112
7.4	Organometallic Compounds of Scandium . . . . .	114
7.5	Yttrium . . . . .	114
7.6	Promethium . . . . .	115
<b>8</b>	<b>The Lanthanides and Scandium in Organic Chemistry . . . . .</b>	<b>121</b>
8.1	Introduction . . . . .	121
8.2	Cerium(IV) Compounds . . . . .	121
8.2.1	Oxidation of Aromatics . . . . .	121
8.2.2	Oxidation of Alkenes . . . . .	123
8.2.3	Oxidation of Alcohols . . . . .	123

8.3	Samarium(II) Iodide, $\text{SmI}_2$ . . . . .	124
8.3.1	Reduction of Halogen Compounds . . . . .	124
8.3.2	Reduction of $\alpha$ -Heterosubstituted Ketones . . . . .	124
8.3.3	Reductions of Carbonyl Groups . . . . .	124
8.3.4	Barbier Reactions . . . . .	126
8.3.5	Reformatsky Reactions . . . . .	127
8.4	Lanthanide $\beta$ -Diketonates as Diels–Alder Catalysts . . . . .	127
8.4.1	Hetero-Diels–Alder Reactions . . . . .	128
8.5	Cerium(III) Chloride and Organocerium Compounds . . . . .	128
8.6	Cerium(III) Chloride and Metal Hydrides . . . . .	130
8.7	Scandium Triflate and Lanthanide Triflates . . . . .	131
8.7.1	Friedel–Crafts Reactions . . . . .	131
8.7.2	Diels–Alder Reactions . . . . .	132
8.7.3	Mannich Reactions . . . . .	132
8.7.4	Imino-Diels–Alder Reactions . . . . .	133
8.8	Alkoxides and Aryloxides . . . . .	134
8.9	Lanthanide Metals . . . . .	135
8.10	Organometallics and Catalysis . . . . .	136
<b>9</b>	<b>Introduction to the Actinides . . . . .</b>	<b>145</b>
9.1	Introduction and Occurrence of the Actinides . . . . .	145
9.2	Synthesis . . . . .	145
9.3	Extraction of Th, Pa, and U . . . . .	147
9.3.1	Extraction of Thorium . . . . .	147
9.3.2	Extraction of Protactinium . . . . .	148
9.3.3	Extraction and Purification of Uranium . . . . .	148
9.4	Uranium Isotope Separation . . . . .	148
9.4.1	Gaseous Diffusion . . . . .	148
9.4.2	Gas Centrifuge . . . . .	148
9.4.3	Electromagnetic Separation . . . . .	149
9.4.4	Laser Separation . . . . .	149
9.5	Characteristics of the Actinides . . . . .	149
9.6	Reduction Potentials of the Actinides . . . . .	150
9.7	Relativistic Effects . . . . .	152
<b>10</b>	<b>Binary Compounds of the Actinides . . . . .</b>	<b>155</b>
10.1	Introduction . . . . .	155
10.2	Halides . . . . .	155
10.2.1	Syntheses . . . . .	156
10.2.2	Structure Types . . . . .	158
10.3	Thorium Halides . . . . .	159
10.4	Uranium Halides . . . . .	160
10.4.1	Uranium(VI) Compounds . . . . .	161
10.4.2	Uranium(V) Compounds . . . . .	161
10.4.3	Uranium (IV) Compounds . . . . .	161
10.4.4	Uranium(III) Compounds . . . . .	163
10.4.5	Uranium Hexafluoride and Isotope Separation . . . . .	163

10.5	The Actinide Halides (Ac–Am) excluding U and Th . . . . .	165
10.5.1	Actinium . . . . .	165
10.5.2	Protactinium . . . . .	165
10.5.3	Neptunium . . . . .	166
10.5.4	Plutonium . . . . .	166
10.5.5	Americium . . . . .	167
10.6	Halides of the Heavier Transactinides . . . . .	168
10.6.1	Curium(III) Chloride . . . . .	168
10.6.2	Californium(III) Chloride, Californium(III) Iodide, and Californium(II) Iodide . . . . .	168
10.6.3	Einsteinium(III) Chloride . . . . .	168
10.7	Oxides . . . . .	169
10.7.1	Thorium Oxide . . . . .	169
10.7.2	Uranium Oxides . . . . .	169
10.8	Uranium Hydride $\text{UH}_3$ . . . . .	170
10.9	Oxyhalides . . . . .	170
<b>11</b>	<b>Coordination Chemistry of the Actinides . . . . .</b>	<b>173</b>
11.1	Introduction . . . . .	173
11.2	General Patterns in the Coordination Chemistry of the Actinides . . . . .	173
11.3	Coordination Numbers in Actinide Complexes . . . . .	174
11.4	Types of Complex Formed . . . . .	174
11.5	Uranium and Thorium Chemistry . . . . .	175
11.5.1	Uranyl Complexes . . . . .	175
11.5.2	Coordination Numbers and Geometries in Uranyl Complexes . . . . .	177
11.5.3	Some Other Complexes . . . . .	178
11.5.4	Uranyl Nitrate and its Complexes; their Role in Processing Nuclear Waste . . . . .	179
11.5.5	Nuclear Waste Processing . . . . .	179
11.6	Complexes of the Actinide(IV) Nitrates and Halides . . . . .	180
11.6.1	Thorium Nitrate Complexes . . . . .	180
11.6.2	Uranium(IV) Nitrate Complexes . . . . .	180
11.6.3	Complexes of the Actinide(IV) Halides . . . . .	181
11.7	Thiocyanates . . . . .	183
11.8	Amides, Alkoxides and Thiolates . . . . .	184
11.8.1	Amide Chemistry . . . . .	184
11.8.2	Alkoxides and Aryloxides . . . . .	185
11.9	Chemistry of Actinium . . . . .	186
11.10	Chemistry of Protactinium . . . . .	187
11.11	Chemistry of Neptunium . . . . .	188
11.11.1	Complexes of Neptunium . . . . .	188
11.12	Chemistry of Plutonium . . . . .	189
11.12.1	Aqueous Chemistry . . . . .	189
11.12.2	The Stability of the Oxidation States of Plutonium . . . . .	190
11.12.3	Coordination Chemistry of Plutonium . . . . .	191
11.12.4	Plutonium in the Environment . . . . .	193
11.13	Chemistry of Americium and Subsequent Actinides . . . . .	195
11.13.1	Potentials . . . . .	195
11.14	Chemistry of the Later Actinides . . . . .	196

<b>12</b>	<b>Electronic and Magnetic Properties of the Actinides</b>	201
12.1	Introduction	201
12.2	Absorption Spectra	202
12.2.1	Uranium(VI) – $\text{UO}_2^{2+}$ – $f^0$	202
12.2.2	Uranium(V) – $f^1$	203
12.2.3	Uranium(IV) – $f^2$	204
12.2.4	Spectra of the Later Actinides	206
12.3	Magnetic Properties	207
<b>13</b>	<b>Organometallic Chemistry of the Actinides</b>	209
13.1	Introduction	209
13.2	Simple $\sigma$ -Bonded Organometallics	209
13.3	Cyclopentadienyls	211
13.3.1	Oxidation State (VI)	211
13.3.2	Oxidation State (V)	211
13.3.3	Oxidation State (IV)	211
13.3.4	Oxidation State (III)	214
13.4	Compounds of the Pentamethylcyclopentadienyl Ligand ( $\text{C}_5\text{Me}_5 = \text{Cp}^*$ )	215
13.4.1	Oxidation State(IV)	215
13.4.2	Cationic Species and Catalysts	216
13.4.3	Hydrides	217
13.4.4	Oxidation State (III)	218
13.5	Tris(pentamethylcyclopentadienyl) Systems	219
13.6	Other Metallacycles	219
13.7	Cyclooctatetraene Dianion Compounds	219
13.8	Arene Complexes	221
13.9	Carbonyls	222
<b>14</b>	<b>Synthesis of the Transactinides and their Chemistry</b>	225
14.1	Introduction	225
14.2	Finding New Elements	226
14.3	Synthesis of the Transactinides	226
14.4	Naming the Transactinides	229
14.5	Predicting Electronic Arrangements	230
14.6	Identifying the Elements	230
14.7	Predicting Chemistry of the Transactinides	233
14.8	What is known about the Chemistry of the Transactinides	234
14.8.1	Element 104	234
14.8.2	Element 105	234
14.8.3	Element 106	234
14.8.4	Element 107	235
14.8.5	Element 108	235
14.9	And the Future?	236
	<b>Bibliography</b>	237
	<b>Index</b>	253

# Preface

This book is aimed at providing a sound introduction to the chemistry of the lanthanides, actinides and transactinides to undergraduate students. I hope that it will also be of value to teachers of these courses. Whilst not being anything resembling a comprehensive monograph, it does attempt to give a factual basis to the area, and the reader can use a fairly comprehensive bibliography to range further.

Since I wrote a previous book in this area (1991), the reader may wonder why on earth I have bothered again. The world of f-block chemistry has moved on. It is one of active and important research, with names like Bünzli, Evans, Ephritikhine, Lappert, Marks and Parker familiar world-wide (I am conscious of names omitted). Not only have several more elements been synthesized (and claims made for others), but lanthanides and their compounds are routinely employed in many areas of synthetic organic chemistry; gadolinium compounds find routine application in MRI scans; and there are other spectroscopic applications, notably in luminescence. Whilst some areas are hardly changed, at this level at least (e.g. actinide magnetism and spectroscopy), a lot more compounds have been described, accounting for the length of the chapters on coordination and organometallic chemistry. I have tried to spell out the energetics of lanthanide chemistry in more detail, whilst I have provided some end-of-chapter questions, of variable difficulty, which may prove useful for tutorials. I have supplied most, but not all, of the answers to these (my answers, which are not always definitive).

It is a pleasure to thank all those who have contributed to the book: Professor Derek Woollins, for much encouragement at different stages of the project; Professor James Anderson, for many valuable comments on Chapter 8; Martyn Berry, who supplied valuable comment on early versions of several chapters; to Professors Michel Ephritikhine, Allan White and Jack Harrowfield, and Dr J.A.G. Williams, and many others, for exchanging e-mails, correspondence and ideas. I'm very grateful to Dr Mary P. Neu for much information on plutonium. The staff of the Libraries of the Chemistry Department of Cambridge University and of the Royal Society of Chemistry, as well as the British Library, have been quite indispensable in helping with access to the primary literature. I would also wish to thank a number of friends – once again Dr Alan Hart, who got me interested in lanthanides in the first place; Professor James Anderson (again), Dr Andrew Platt, Dr John Fawcett, and Professor Paul Raithby, for continued research collaboration and obtaining spectra and structures from unpromising crystals, so that I have kept a toe-hold in the area. Over the last 8 years, a number of Uppingham 6th form students have contributed to my efforts in lanthanide coordination chemistry – John Bower, Oliver Noy, Rachel How, Vilius Franckevicius, Leon Catallo, Franz Niecknig, Victoria Fisher, Alex Tait and Joanna Harris. Finally, thanks are most certainly due to Dom Paul-Emmanuel Clénet and the Benedictine community of the Abbey of Bec, for continued hospitality during several Augusts when I have been compiling the book.

Simon Cotton





# 1 Introduction to the Lanthanides

By the end of this chapter you should be able to:

- understand that lanthanides differ in their properties from the s- and d-block metals;
- recall characteristic properties of these elements;
- appreciate reasons for their positioning in the Periodic Table;
- understand how the size of the lanthanide ions affects certain properties and how this can be used in the extraction and separation of the elements;
- understand how to obtain pure samples of individual  $\text{Ln}^{3+}$  ions.

## 1.1 Introduction

Lanthanide chemistry started in Scandinavia. In 1794 Johann Gadolin succeeded in obtaining an ‘earth’(oxide) from a black mineral subsequently known as gadolinite; he called the earth yttria. Soon afterwards, M.H. Klaproth, J.J. Berzelius and W. Hisinger obtained ceria, another earth, from cerite. However, it was not until 1839–1843 that the Swede C.G. Mosander first separated these earths into their component oxides; thus ceria was resolved into the oxides of cerium and lanthanum and a mixed oxide ‘didymia’ (a mixture of the oxides of the metals from Pr through Gd). The original yttria was similarly separated into substances called erbia, terbia, and yttria (though some 40 years later, the first two names were to be reversed!). This kind of confusion was made worse by the fact that the newly discovered means of spectroscopic analysis permitted misidentifications, so that around 70 ‘new’ elements were erroneously claimed in the course of the century.

Nor was Mendeleev’s revolutionary Periodic Table a help. When he first published his Periodic Table in 1869, he was able to include only lanthanum, cerium, didymium (now known to have been a mixture of Pr and Nd), another mixture in the form of erbia, and yttrium; unreliable information about atomic mass made correct positioning of these elements in the table difficult. Some had not yet been isolated as elements. There was no way of predicting how many of these elements there would be until Henry Moseley (1887–1915) analysed the X-ray spectra of elements and gave meaning to the concept of atomic number. He showed that there were 15 elements from lanthanum to lutetium (which had only been identified in 1907). The discovery of radioactive promethium had to wait until after World War 2.

It was the pronounced similarity of the lanthanides to each other, especially each to its neighbours (a consequence of their general adoption of the +3 oxidation state in aqueous solution), that caused their classification and eventual separation to be an extremely difficult undertaking.

Subsequently it was not until the work of Bohr and of Moseley that it was known precisely how many of these elements there were. Most current versions of the Periodic Table place lanthanum under scandium and yttrium.

## 1.2 Characteristics of the Lanthanides

The lanthanides exhibit a number of features in their chemistry that differentiate them from the d-block metals. The reactivity of the elements is greater than that of the transition metals, akin to the Group II metals:

1. A very wide range of coordination numbers (generally 6–12, but numbers of 2, 3 or 4 are known).
2. Coordination geometries are determined by ligand steric factors rather than crystal field effects.
3. They form labile ‘ionic’ complexes that undergo facile exchange of ligand.
4. The 4f orbitals in the  $\text{Ln}^{3+}$  ion do not participate directly in bonding, being well shielded by the  $5s^2$  and  $5p^6$  orbitals. Their spectroscopic and magnetic properties are thus largely uninfluenced by the ligand.
5. Small crystal-field splittings and very sharp electronic spectra in comparison with the d-block metals.
6. They prefer anionic ligands with donor atoms of rather high electronegativity (e.g. O, F).
7. They readily form hydrated complexes (on account of the high hydration energy of the small  $\text{Ln}^{3+}$  ion) and this can cause uncertainty in assigning coordination numbers.
8. Insoluble hydroxides precipitate at neutral pH unless complexing agents are present.
9. The chemistry is largely that of one (3+) oxidation state (certainly in aqueous solution).
10. They do not form  $\text{Ln}=\text{O}$  or  $\text{Ln}\equiv\text{N}$  multiple bonds of the type known for many transition metals and certain actinides.
11. Unlike the transition metals, they do not form stable carbonyls and have (virtually) no chemistry in the 0 oxidation state.

## 1.3 The Occurrence and Abundance of the Lanthanides

Table 1.1 presents the abundance of the lanthanides in the earth’s crust and in the solar system as a whole. (Although not in the same units, the values in each list are internally consistent.)

Two patterns emerge from these data. First, that the lighter lanthanides are more abundant than the heavier ones; secondly, that the elements with even atomic number are more abundant than those with odd atomic number. Overall, cerium, the most abundant lanthanide

**Table 1.1** Abundance of the lanthanides

	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y
Crust (ppm)	35	66	9.1	40	0.0	7	2.1	6.1	1.2	4.5	1.3	3.5	0.5	3.1	0.8	31
Solar System (with respect to $10^7$ atoms Si)	4.5	1.2	1.7	8.5	0.0	2.5	1.0	3.3	0.6	3.9	0.9	2.5	0.4	2.4	0.4	40.0

on earth, has a similar crustal concentration to the lighter Ni and Cu, whilst even Tm and Lu, the rarest lanthanides, are more abundant than Bi, Ag or the platinum metals.

The abundances are a consequence of how the elements were synthesized by atomic fusion in the cores of stars with heavy elements only made in supernovae. Synthesis of heavier nuclei requires higher temperature and pressures and so gets progressively harder as the atomic number increases. The odd/even alternation (often referred to as the Oddo–Harkins rule) is again general, and reflects the facts that elements with odd mass numbers have larger nuclear capture cross sections and are more likely to take up another neutron, so elements with odd atomic number (and hence odd mass number) are less common than those with even mass number. Even-atomic-number nuclei are more stable when formed.

## 1.4 Lanthanide Ores

Principal sources (Table 1.2) are the following:

Bastnasite  $\text{LnFCO}_3$ ; Monazite  $(\text{Ln}, \text{Th})\text{PO}_4$  (richer in earlier lanthanides); Xenotime  $(\text{Y}, \text{Ln})\text{PO}_4$  (richer in later lanthanides). In addition to these, there are Chinese rare earth reserves which amount to over 70% of the known world total, mainly in the form of the ionic ores from southern provinces. These Chinese ion-absorption ores, weathered granites with lanthanides adsorbed onto the surface of aluminium silicates, are in some cases low in cerium and rich in the heavier lanthanides (Longnan) whilst the Xunwu deposits are rich in the lighter metals; the small particle size makes them easy to mine. The Chinese ores have made them a leading player in lanthanide chemistry.

**Table 1.2** Typical abundance of the lanthanides in ores<sup>a</sup>

%	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y
Monazite	20	43	4.5	16	0	3	0.1	1.5	0.05	0.6	0.05	0.2	0.02	0.1	0.02	2.5
Bastnasite	33.2	49.1	4.3	12	0	0.8	0.12	0.17	<b>160</b>	<b>310</b>	<b>50</b>	<b>35</b>	<b>8</b>	<b>6</b>	<b>1</b>	0.1
Xenotime	0.5	5	0.7	2.2	0	1.9	0.2	4	1	8.6	2	5.4	0.9	6.2	0.4	60.0

<sup>a</sup> Bold values are in ppm.

## 1.5 Extracting and Separating the Lanthanides

These two processes are not necessarily coterminous. Whilst electronic, optical and magnetic applications require individual pure lanthanides, the greatest quantity of lanthanides is used as mixtures, e.g. in mischmetal or oxide catalysts.

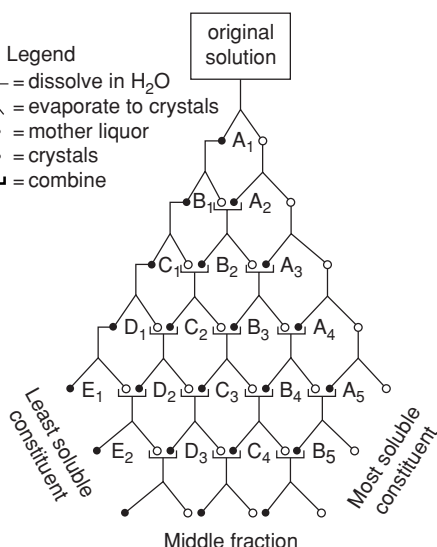
### 1.5.1 Extraction

After initial concentration by crushing, grinding and froth flotation, bastnasite is treated with 10% HCl to remove calcite, by which time the mixture contains around 70% lanthanide oxides. This is roasted to oxidize the cerium content to  $\text{Ce}^{\text{IV}}$ ; on further extraction with HCl, the Ce remains as  $\text{CeO}_2$ , whilst the lanthanides in the (+3) state dissolve as a solution of the chlorides.

Monazite is usually treated with NaOH at 150 °C to remove phosphate as  $\text{Na}_3\text{PO}_4$ , leaving a mixture of the hydrated oxides, which are dissolved in boiling HCl at pH 3.5, separating the lanthanides from insoluble  $\text{ThO}_2$ . Sulfuric acid can also be used to dissolve the lanthanides.

### 1.5.2 Separating the Lanthanides

These can be divided into four types: chemical separations, fractional crystallization, ion-exchange methods and solvent extraction. Of these, only the last-named is used on a commercial scale (apart from initial separation of cerium). Chemical separations rely on using stabilities of unusual oxidation states; thus  $\text{Eu}^{2+}$  is the only ion in that oxidation state formed on reduction by zinc amalgam and can then be precipitated as  $\text{EuSO}_4$  (note the similarity with heavier Group 2 metals). Repeated (and tedious) fractional crystallization, which made use of slight solubility differences between the salts of neighbouring lanthanides, such as the bromates  $\text{Ln}(\text{BrO}_3)_3 \cdot 9\text{H}_2\text{O}$ , ethyl sulfates and double nitrates, were once the only possible way of obtaining pure lanthanides, as with the 15 000 recrystallizations carried out by the American C. James to get pure thulium bromate (1911) (Figure 1.1 indicates the principle of this method).

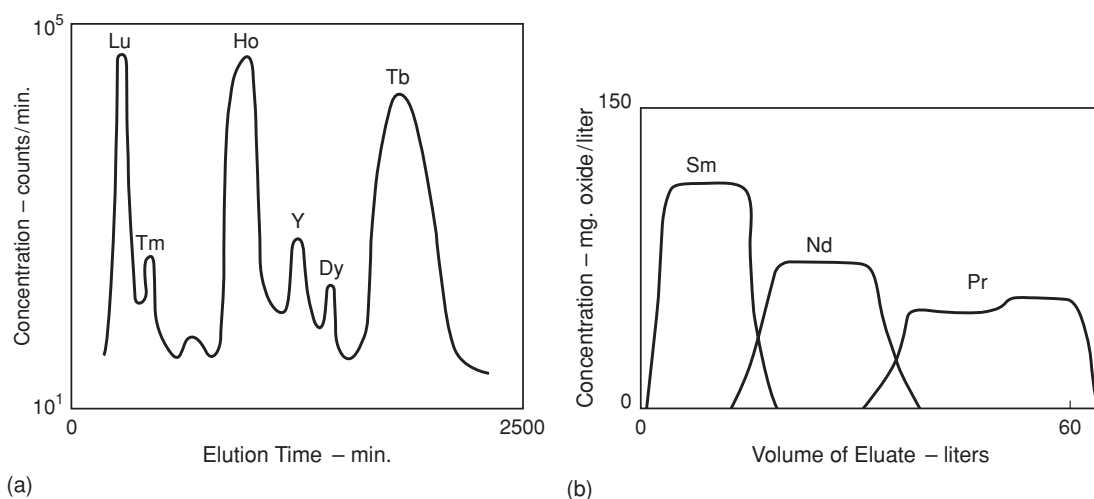


**Figure 1.1**

Diagrammatic representation of the system of fractional crystallization used to separate salts of the rare-earth elements (reproduced with permission from D.M. Yost, H. Russell and C.S. Garner, *The Rare Earth Elements and their Compounds*, John Wiley, 1947.)

Ion-exchange chromatography is not of real commercial importance for large-scale production, but historically it was the method by which fast high-purity separation of the lanthanides first became feasible. As radioactive lanthanide isotopes are important fission products of the fission of  $^{235}\text{U}$  and therefore need to be separated from uranium, and because the actinides after plutonium tend to resemble the lanthanides, the development of the technique followed on the Manhattan project. It was found that if  $\text{Ln}^{3+}$  ions were adsorbed at the top of a cation-exchange resin, then treated with a complexing agent such as buffered citric acid, then the cations tended to be eluted in reverse atomic number order (Figure 1.2a); the anionic ligand binds most strongly to the heaviest (and smallest) cation, which has the highest charge density. A disadvantage of this approach when scaled up to high concentration is that the peaks tend to overlap (Figure 1.2b).

It was subsequently found that amine polycarboxylates such as  $\text{EDTA}^{4-}$  gave stronger complexes and much better separations. In practice, some  $\text{Cu}^{2+}$  ions ('retainer') are added to prevent precipitation of either the free acid  $\text{H}_4\text{EDTA}$  or the lanthanide complex

**Figure 1.2**

(a) Cation-exchange chromatography of lanthanides, (b) overlap of peaks at high concentration. (a) Tracer-scale elution with 5% citrate at pH 3.20 (redrawn from B.H. Ketelle and G.E. Boyd, *J. Am. Chem. Soc.*, 1947, **69**, 2800). (b) Macro-scale elution with 0.1% citrate at pH 5.30 (redrawn from F.H. Spedding, E.I. Fulmer, J.E. Powell, and T.A. Butler, *J. Am. Chem. Soc.*, 1950, **72**, 2354). Reprinted with permission of the American Chemical Society ©1978.

HLn(EDTA).*x*H<sub>2</sub>O on the resin. The major disadvantage of this method is that it is a slow process for large-scale separations.

Solvent extraction has come to be used for the initial stage of the separation process, to give material with up to 99.9% purity. In 1949, it was found that Ce<sup>4+</sup> could readily be separated from Ln<sup>3+</sup> ions by extraction from a solution in nitric acid into tributyl phosphate [(BuO)<sub>3</sub>PO]. Subsequently the process was extended to separating the lanthanides, using a non-polar organic solvent such as kerosene and an extractant such as (BuO)<sub>3</sub>PO or bis (2-ethylhexyl)phosphinic acid [[C<sub>4</sub>H<sub>9</sub>CH(C<sub>2</sub>H<sub>5</sub>)]<sub>2</sub>P=O(OH)] to extract the lanthanides from aqueous nitrate solutions. The heavier lanthanides form complexes which are more soluble in the aqueous layer. After the two immiscible solvents have been agitated together and separated, the organic layer is treated with acid and the lanthanide extracted. The solvent is recycled and the aqueous layer put through further stages.

For a lanthanide Ln<sub>A</sub> distributed between two phases, a distribution coefficient *D*<sub>A</sub> is defined:

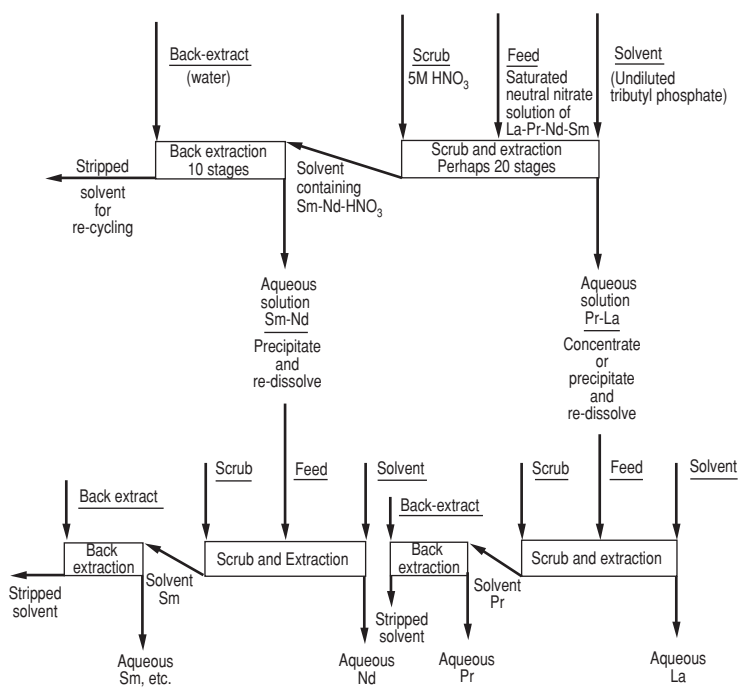
$$D_A = [\text{Ln}_A \text{ in organic phase}] / [\text{Ln}_A \text{ in aqueous phase}]$$

For two lanthanides Ln<sub>A</sub> and Ln<sub>B</sub> in a mixture being separated, a separation factor β<sub>B</sub><sup>A</sup> can be defined, where

$$\beta_B^A = D_A / D_B$$

β is very close to unity for two adjacent lanthanides in the Periodic Table (obviously, the larger β is, the better the separation).

In practice this process is run using an automated continuous counter-current circuit in which the organic solvent flows in the opposite direction to the aqueous layer containing the lanthanides. An equilibrium is set up between the lanthanide ions in the aqueous phase and the organic layer, with there tending to be a relative enhancement of the concentration of the heavier lanthanides in the organic layer. Because the separation between adjacent

**Figure 1.3**

Schematic diagram of lanthanide separation by solvent extraction. From R.J. Callow, *The Rare Earth Industry*, Pergamon, 1966; reproduced by permission.

lanthanides in each exchange is relatively slight, over a thousand exchanges are used (see Figure 1.3). This method affords lanthanides of purity up to the 99.9% purity level and is thus well suited to large-scale separation, the products being suited to ordinary chemical use. However, for electronic or spectroscopic use ('phosphor grade') 99.999% purity is necessary, and currently ion-exchange is used for final purification to these levels. The desired lanthanides are precipitated as the oxalate or hydroxide and converted into the oxides (the standard starting material for many syntheses) by thermal decomposition.

Various other separation methods have been described, one recent one involving the use of supercritical carbon dioxide at 40 °C and 100 atm to convert the lanthanides into their carbonates whilst the quadrivalent metals (e.g. Th and Ce) remain as their oxides.

## 1.6 The Position of the Lanthanides in the Periodic Table

As already mentioned, neither Mendeleev nor his successors could 'place' the lanthanides in the Periodic Table. Not only was there no recognizable atomic theory until many years afterwards, but, more relevant to how groupings of elements were made in those days, there was no comparable block of elements for making comparisons. The lanthanides were *sui generis*. The problem was solved by the combined (but separate) efforts of Moseley and Bohr, the former showing that La–Lu was composed of 15 elements with atomic numbers from 57 to 71, whilst the latter concluded that the fourth quantum shell could accommodate 32 electrons, and that the lanthanides were associated with placing electrons into the 4f orbitals.

The Periodic Table places elements in atomic number order, with the lanthanides falling between barium (56) and hafnium (72). For reasons of space, most present-day Periodic Tables are presented with Groups IIA and IVB (2 and 4) separated only by the Group IIIB (3) elements. Normally La (and Ac) are grouped with Sc and Y, but arguments have been advanced for an alternative format, in which Lu (and Lr) are grouped with Sc and Y (see e.g. W.B. Jensen, *J. Chem. Educ.*, 1982, **59**, 634) on the grounds that trends in properties (e.g. atomic radius, I.E., melting point) in the block Sc-Y-Lu parallel those in the Group Ti-Zr-Hf rather closely, and that there are resemblances in the structures of certain binary compounds. Certainly on size grounds, Lu resembles Y and Sc (it is intermediate in size between them) rather more than does La, owing to the effects of the ‘lanthanide contraction’. The resemblances between Sc and Lu are, however, by no means complete.

## 1.7 The Lanthanide Contraction

The basic concept is that there is a decrease in radius of the lanthanide ion  $\text{Ln}^{3+}$  on crossing the series from La to Lu. This is caused by the poor screening of the 4f electrons. This causes neighbouring lanthanides to have similar, but not identical, properties, and is discussed in more detail in Section 2.4.

**Question 1.1** Using the information you have been given in Section 1.2, draw up a table comparing (in three columns) the characteristic features of the s-block metals (use group 1 as typical) and the d-block transition metals.

**Answer 1.1** see Table 1.3 for one such comparison.

**Table 1.3** Comparison of 4f, 3d and Group I metals

	4f	3d	Group I
Electron configurations of ions	Variable	Variable	Noble gas
Stable oxidation states	Usually +3	Variable	1
Coordination numbers in complexes	Commonly 8–10	Usually 6	Often 4–6
Coordination polyhedra in complexes	Minimise repulsion	Directional	Minimise repulsion
Trends in coordination numbers	Often constant in block	Often constant in block	Increase down group
Donor atoms in complexes	‘Hard’ preferred	‘Hard’ and ‘soft’	‘Hard’ preferred
Hydration energy	High	Usually moderate	Low
Ligand exchange reactions	Usually fast	Fast and slow	Fast
Magnetic properties of ions	Independent of environment	Depends on environment and ligand field	None
Electronic spectra of ions	Sharp lines	Broad lines	None
Crystal field effects in complexes	Weak	Strong	None
Organometallic compounds	Usually ionic, some with covalent character	Covalently bonded	Ionically bonded
Organometallics in low oxidation states	Few	Common	None
Multiply bonded atoms in complexes	None	Common	None





## 2 The Lanthanides – Principles and Energetics

By the end of this chapter you should be able to:

- recognise the difference between f-orbitals and other types of orbitals;
- understand that they are responsible for the particular properties of the lanthanides;
- give the electron configurations of the lanthanide elements and  $\text{Ln}^{3+}$  ions;
- explain the reason for the lanthanide contraction;
- understand the effect of the lanthanide contraction upon properties of the lanthanides and subsequent elements;
- explain patterns in properties such as ionization and hydration energies;
- recall that lanthanides behave similarly when there is no change in the 4f electron population, but that they differ when the change involves a change in the number of 4f electrons;
- relate the stability of oxidation states to the ionization energies;
- calculate enthalpy changes for the formation of the aqua ions and of the lanthanide halides and relate these to the stability of particular compounds.

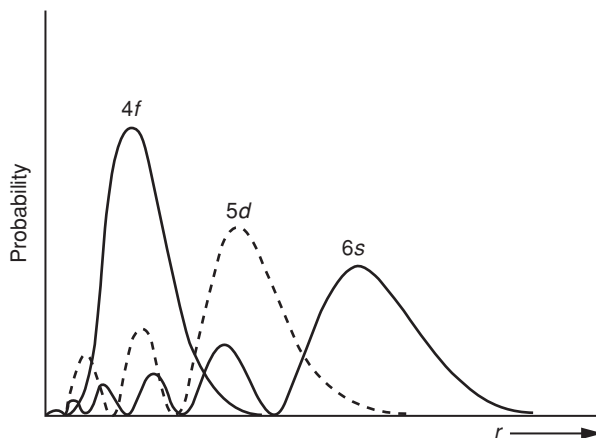
### 2.1 Electron Configurations of the Lanthanides and f Orbitals

The lanthanides (and actinides) are those in which the 4f (and 5f) orbitals are gradually filled. At lanthanum, the 5d subshell is lower in energy than 4f, so lanthanum has the electron configuration  $[\text{Xe}] 6s^2 5d^1$  (Table 2.1).

As more protons are added to the nucleus, the 4f orbitals contract rapidly and become more stable than the 5d (as the 4f orbitals penetrate the ‘xenon core’ more) (see Figure 2.1), so that Ce has the electron configuration  $[\text{Xe}] 6s^2 5d^1 4f^1$  and the trend continues with Pr having the arrangement  $[\text{Xe}] 6s^2 4f^3$ . This pattern continues for the metals Nd–Eu, all of which have configurations  $[\text{Xe}] 6s^2 4f^n$  ( $n = 4\text{--}7$ ). After europium, the stability of the half-filled f subshell is such that the next electron is added to the 5d orbital, Gd being  $[\text{Xe}] 6s^2 5d^1 4f^7$ ; at terbium, however, the earlier pattern is resumed, with Tb having the configuration  $[\text{Xe}] 6s^2 4f^9$ , and succeeding elements to ytterbium being  $[\text{Xe}] 6s^2 4f^n$  ( $n = 10\text{--}14$ ). The last lanthanide, lutetium, where the 4f subshell is now filled, is predictably  $[\text{Xe}] 6s^2 5d^1 4f^{14}$ .

**Table 2.1** Electron configurations of the lanthanides and their common ions

	Atom	$\text{Ln}^{3+}$	$\text{Ln}^{4+}$	$\text{Ln}^{2+}$
La	$[\text{Xe}] 5d^1 6s^2$	$[\text{Xe}]$		
Ce	$[\text{Xe}] 4f^1 5d^1 6s^2$	$[\text{Xe}] 4f^1$	$[\text{Xe}]$	
Pr	$[\text{Xe}] 4f^3 6s^2$	$[\text{Xe}] 4f^2$	$[\text{Xe}] 4f^1$	
Nd	$[\text{Xe}] 4f^4 6s^2$	$[\text{Xe}] 4f^3$	$[\text{Xe}] 4f^2$	$[\text{Xe}] 4f^4$
Pm	$[\text{Xe}] 4f^5 6s^2$	$[\text{Xe}] 4f^4$		
Sm	$[\text{Xe}] 4f^6 6s^2$	$[\text{Xe}] 4f^5$		$[\text{Xe}] 4f^6$
Eu	$[\text{Xe}] 4f^7 6s^2$	$[\text{Xe}] 4f^6$		$[\text{Xe}] 4f^7$
Gd	$[\text{Xe}] 4f^7 5d^1 6s^2$	$[\text{Xe}] 4f^7$		
Tb	$[\text{Xe}] 4f^9 6s^2$	$[\text{Xe}] 4f^8$	$[\text{Xe}] 4f^7$	
Dy	$[\text{Xe}] 4f^{10} 6s^2$	$[\text{Xe}] 4f^9$	$[\text{Xe}] 4f^8$	$[\text{Xe}] 4f^{10}$
Ho	$[\text{Xe}] 4f^{11} 6s^2$	$[\text{Xe}] 4f^{10}$		
Er	$[\text{Xe}] 4f^{12} 6s^2$	$[\text{Xe}] 4f^{11}$		
Tm	$[\text{Xe}] 4f^{13} 6s^2$	$[\text{Xe}] 4f^{12}$		$[\text{Xe}] 4f^{13}$
Yb	$[\text{Xe}] 4f^{14} 6s^2$	$[\text{Xe}] 4f^{13}$		$[\text{Xe}] 4f^{14}$
Lu	$[\text{Xe}] 4f^{14} 5d^1 6s^2$	$[\text{Xe}] 4f^{14}$		
Y	$[\text{Kr}] 4d^1 5s^2$	$[\text{Kr}]$		

**Figure 2.1**

The radial part of the hydrogenic wave functions for the 4f, 5d and 6s orbitals of cerium (after H.G. Friedman *et al. J. Chem. Educ.* 1964, **41**, 357). Reproduced by permission of the American Chemical Society © 1964.

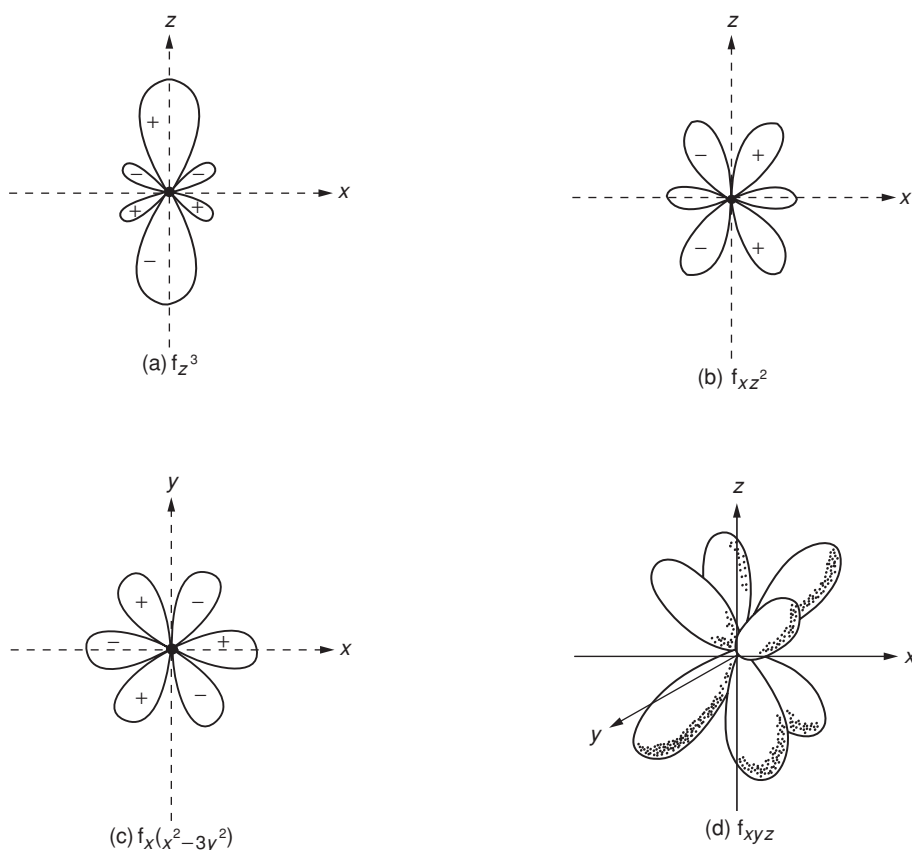
## 2.2 What do f Orbitals Look Like?

They are generally represented in one of two ways, either as a cubic set, or as a general set, depending upon which way the orbitals are combined. The cubic set comprises  $f_{xyz}$ ;  $f_{z(x^2-y^2)}$ ,  $f_{z(y^2-z^2)}$  and  $f_{y(z^2-x^2)}$ ;  $f_{z^3}$ ,  $f_{x^3}$  and  $f_{y^3}$ .

The general set, more useful in non-cubic environments, uses a different combination:  $f_{z^3}$ ;  $f_{xz^2}$  and  $f_{yz^2}$ ;  $f_{xyz}$ ;  $f_{z(x^2-y^2)}$ ,  $f_{x(x^2-3y^2)}$  and  $f_{y(3x^2-y^2)}$ ; Figure 2.2 shows the general set.

## 2.3 How f Orbitals affect Properties of the Lanthanides

The 4f orbitals penetrate the xenon core appreciably. Because of this, they cannot overlap with ligand orbitals and therefore do not participate significantly in bonding. As a result of

**Figure 2.2**

(a)  $f_z^3$ , ( $f_x^3$  and  $f_y^3$  are similar, extending along the  $x$ - and  $y$ -axes respectively); (b)  $f_{xz^2}$ , ( $f_{yz^2}$  is similar, produced by a  $90^\circ$  rotation about the  $z$ -axis); (c)  $f_{x(x^2-3y^2)}$ ,  $f_{y(3x^2-y^2)}$  is similar, formed by a  $90^\circ$  clockwise rotation round the  $z$ -axis); (d)  $f_{xyz}$ , ( $f_{xz^2-y^2}$ ),  $f_{y(z^2-y^2)}$  and  $f_{z(x^2-y^2)}$  are produced by a  $45^\circ$  rotation about the  $x$ ,  $y$  and  $z$ -axes respectively). The cubic set comprises  $f_x^3$ ,  $f_y^3$ ,  $f_z^3$ ,  $f_{xyz}$ ,  $f_{x(z^2-y^2)}$ ,  $f_{y(z^2-x^2)}$  and  $f_{z(x^2-y^2)}$ ; the general set is made of  $f_z^3$ ,  $f_{xz^2}$ ,  $f_{yz^2}$ ,  $f_{xyz}$ ,  $f_{z(x^2-y^2)}$ ,  $f_{x(x^2-3y^2)}$  and  $f_{y(3x^2-y^2)}$ . (Reproduces with permission from S.A. Cotton, *Lanthanides and Actinides*, Macmillan, 1991).

their isolation from the influence of the ligands, crystal-field effects are very small (and can be regarded as a perturbation on the free-ion states) and thus electronic spectra and magnetic properties are essentially unaffected by environment. The ability to form  $\pi$  bonds is also absent, and thus there are none of the  $M=O$  or  $M\equiv N$  bonds found for transition metals (or, indeed, certain early actinides). The organometallic chemistry is appreciably different from that of transition metals, too.

## 2.4 The Lanthanide Contraction

As the series La–Lu is traversed, there is a decrease in both the atomic radii and in the radii of the  $Ln^{3+}$  ions, more markedly at the start of the series. The 4f electrons are ‘inside’ the 5s and 5p electrons and are core-like in their behaviour, being shielded from the ligands, thus taking no part in bonding, and having spectroscopic and magnetic properties largely independent of environment. The 5s and 5p orbitals penetrate the 4f subshell and are not shielded from

increasing nuclear charge, and hence because of the increasing effective nuclear charge they contract as the atomic number increases. Some part (but only a small fraction) of this effect has also been ascribed to relativistic effects. The lanthanide contraction is sometimes spoken of as if it were unique. It is not, at least in the way that the term is usually used. Not only does a similar phenomenon take place with the actinides (and here relativistic effects are much more responsible) but contractions are similarly noticed on crossing the first and second long periods (Li–Ne; Na–Ar) not to mention the d-block transition series. However, as will be seen, because of a combination of circumstances, the lanthanides adopt primarily the (+3) oxidation state in their compounds, and therefore demonstrate the steady and subtle changes in properties in a way that is not observed in other blocks of elements.

The lanthanide contraction has a knock-on effect in the elements in the 5d transition series. It would naturally be expected that the 5d elements would show a similar increase in size over the 4d transition elements to that which the 4d elements demonstrate over the 3d metals. However, it transpires that the ‘lanthanide contraction’ cancels this out, almost exactly, and this has pronounced effects on the chemistry, e.g. Pd resembling Pt rather than Ni, Hf is extremely similar to Zr.

## 2.5 Electron Configurations of the Lanthanide Elements and of Common Ions

The electronic arrangements of the lanthanide atoms have already been mentioned (Section 2.1 and Table 2.1) where it can be seen that in general the ECs of the atoms are [Xe]  $4f^n 5d^0 6s^2$ , the exceptions being La and Ce, where the 4f orbitals have not contracted sufficiently to bring the energy of the 4f electrons below that of the 5d electrons; Gd, where the effect of the half-filled 4f subshell dominates; and Lu, the 4f subshell having already been filled at Yb.

In forming the ions, electrons are removed first from the 6s and 5d orbitals (rather reminiscent of the case of the transition metals, where they are removed from 4s before they are taken from 3d), so that all the  $\text{Ln}^{3+}$  ions have [Xe]  $4f^n$  arrangements.

## 2.6 Patterns in Ionization Energies

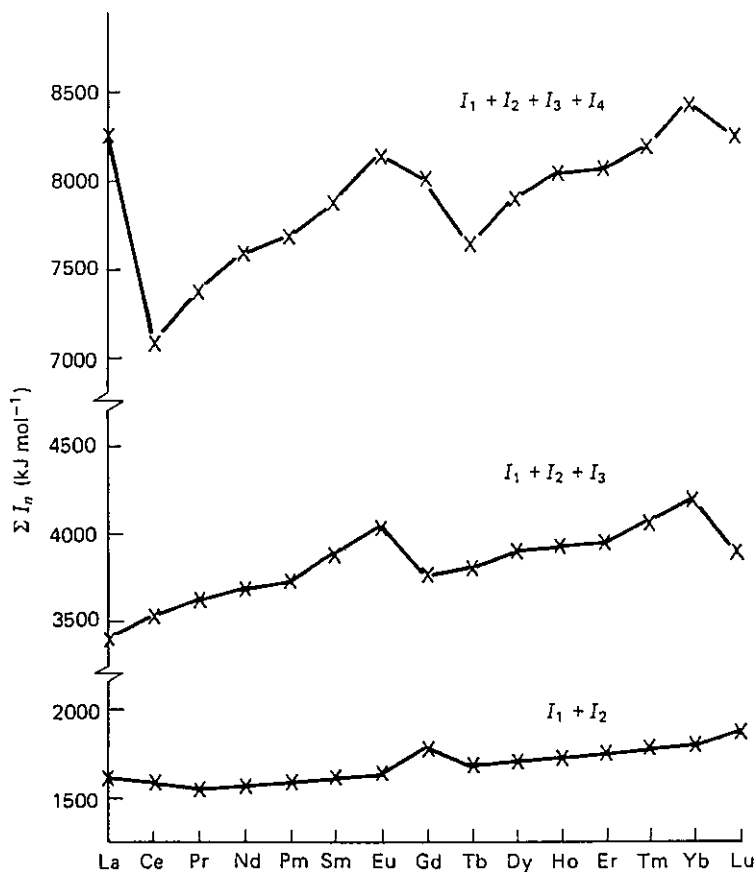
The values of the first four ionization energies for the lanthanides (and yttrium) are listed in Table 2.2.

As usual, for a particular element,  $I_4 > I_3 > I_2 > I_1$ , as the electron being removed is being taken from an ion with an increasingly positive charge, affording greater electrostatic attraction. Yttrium has greater ionization energies than the lanthanides as there is one fewer filled shell, and decreased distance effects outweigh the effect of the reduced nuclear charge.

There is in general a tendency for ionization energies to increase on crossing the series but it is irregular. The low  $I_3$  values for gadolinium and lutetium, where the one electron removed comes from a d orbital, not an f orbital, and the high  $I_3$  value for Eu and Yb show some correlation with the stabilizing effects of half-filled and filled f sub shells. Results can be presented diagrammatically as cumulative ionization energies (Figure 2.3). These diagrams demonstrate at a glance the effect of the alternately high and low values of  $I_3$  for the elements Eu and Gd, influencing the respective stabilities of the +2 and +3 states of these elements, similarly illustrated by the neighbours Yb and Lu. The low  $I_4$  value for Ce (and to some extent for Pr and Tb) can be correlated with the accessibility of the  $\text{Ce}^{4+}$  ion.

**Table 2.2** Ionization Energies (kJ/mole)

	$I_1$	$I_2$	$I_3$	$I_4$	$I_1 + I_2$	$I_1 + I_2 + I_3$	$I_1 + I_2 + I_3 + I_4$
La	538	1067	1850	4819	1605	3455	8274
Ce	527	1047	1949	3547	1574	3523	7070
Pr	523	1018	2086	3761	1541	3627	7388
Nd	529	1035	2130	3899	1564	3694	7593
Pm	536	1052	2150	3970	1588	3738	7708
Sm	543	1068	2260	3990	1611	3871	7990
Eu	546	1085	2404	4110	1631	4035	8145
Gd	593	1167	1990	4250	1760	3750	8000
Tb	564	1112	2114	3839	1676	3790	7629
Dy	572	1126	2200	4001	1698	3898	7899
Ho	581	1139	2204	4110	1720	3924	8034
Er	589	1151	2194	4115	1740	3934	8049
Tm	597	1163	2285	4119	1760	4045	8164
Yb	603	1176	2415	4220	1779	4194	8414
Lu	523	1340	2033	4360	1863	3896	8256
Y	616	1181	1980	5963	1797	3777	9740

**Figure 2.3**

Cumulative ionization energies across the lanthanide Series (reproduced by permission of Macmillan from S.A. Cotton, *Lanthanides and Actinides*, Macmillan, 1991).

## 2.7 Atomic and Ionic Radii

These are listed in Table 2.3 and shown in Figure 2.4. It will be seen that the atomic radii exhibit a smooth trend across the series with the exception of the elements europium and ytterbium. Otherwise the lanthanides have atomic radii intermediate between those of barium in Group 2A and hafnium in Group 4A, as expected if they are represented as  $\text{Ln}^{3+}(\text{e}^-)_3$ . Because the screening ability of the f electrons is poor, the effective nuclear charge experienced by the outer electrons increases with increasing atomic number, so that the atomic radius would be expected to decrease, as is observed. Eu and Yb are exceptions to this; because of the tendency of these elements to adopt the (+2) state, they have the structure  $[\text{Ln}^{2+}(\text{e}^-)_2]$  with consequently greater radii, rather similar to barium. In contrast, the ionic radii of the  $\text{Ln}^{3+}$  ions exhibit a smooth decrease as the series is crossed.

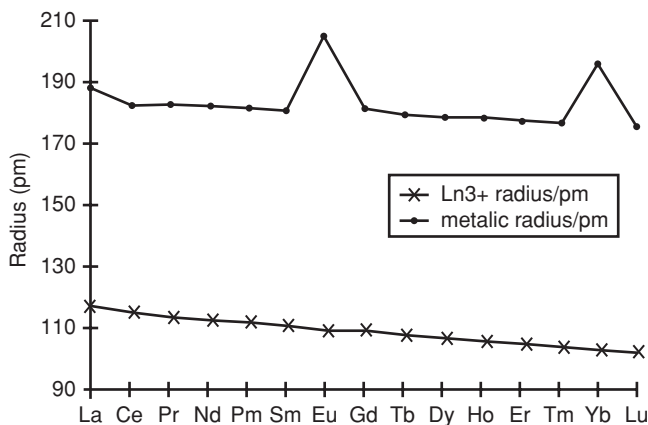
The patterns in radii exemplify a principle enunciated by D.A. Johnson: ‘The lanthanide elements behave similarly in reactions in which the 4f electrons are conserved, and very differently in reactions in which the number of 4f electrons change’ (*J. Chem. Educ.*, 1980, **57**, 475).

**Table 2.3** Atomic and ionic radii of the lanthanides (pm)

Ba	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf
217.3	187.7	182.5	182.8	182.1	181.0	180.2	204.2	180.2	178.2	177.3	176.6	175.7	174.6	194.0	173.4	156.4
	$\text{La}^{3+}$	$\text{Ce}^{3+}$	$\text{Pr}^{3+}$	$\text{Nd}^{3+}$	$\text{Pm}^{3+}$	$\text{Sm}^{3+}$	$\text{Eu}^{3+}$	$\text{Gd}^{3+}$	$\text{Tb}^{3+}$	$\text{Dy}^{3+}$	$\text{Ho}^{3+}$	$\text{Er}^{3+}$	$\text{Tm}^{3+}$	$\text{Yb}^{3+}$	$\text{Lu}^{3+}$	$\text{Y}^{3+}$
	103.2	101.0	99.0	98.3	97.0	95.8	94.7	93.8	92.3	91.2	90.1	89.0	88.0	86.8	86.1	90.0

## 2.8 Patterns in Hydration Energies (Enthalpies) for the Lanthanide Ions

Table 2.4 shows the hydration energies (enthalpies) for all the 3+ lanthanide ions, and also values for the stablest ions in other oxidation states. Hydration energies fall into a pattern  $\text{Ln}^{4+} > \text{Ln}^{3+} > \text{Ln}^{2+}$ , which can simply be explained on the basis of electrostatic attraction,



**Figure 2.4**

Metallic and ionic radii across the lanthanide series.

$\text{La}^{3+}$	$\text{Ce}^{3+}$	$\text{Pr}^{3+}$	$\text{Nd}^{3+}$	$\text{Pm}^{3+}$	$\text{Sm}^{3+}$	$\text{Eu}^{3+}$	$\text{Gd}^{3+}$	$\text{Tb}^{3+}$	$\text{Dy}^{3+}$	$\text{Ho}^{3+}$	$\text{Er}^{3+}$	$\text{Tm}^{3+}$	$\text{Yb}^{3+}$	$\text{Lu}^{3+}$	$\text{Y}^{3+}$
3278	3326 $\text{Ce}^{4+}$ 6309	3373	3403	3427	3449 $\text{Sm}^{2+}$ 1444	3501 $\text{Eu}^{2+}$ 1458	3517	3559	3567	3623	3637	3664	3706 $\text{Yb}^{2+}$ 1594	3722	3583



**Table 2.5** Enthalpies of formation of lanthanide halides<sup>a</sup>

	LnF <sub>2</sub>	LnF <sub>3</sub>	LnF <sub>4</sub>	LnCl <sub>2</sub>	LnCl <sub>3</sub>	LnCl <sub>4</sub>	LnBr <sub>2</sub>	LnBr <sub>3</sub>	LnI <sub>2</sub>	LnI <sub>3</sub>
La	880	<b>1732</b>	600	520	<b>1073</b>	–480	430	<b>907</b>	320	<b>699</b>
Ce	950	<b>1733</b>	<b>1946</b>	580	<b>1058</b>	820	490	890	380	<b>686</b>
Pr	1050	<b>1712</b>	1690	700	<b>1059</b>	630	610	<b>891</b>	490	<b>678</b>
Nd	1050	<b>1661</b>	1500	<b>707</b>	<b>1042</b>	490	630	<b>873</b>	510	<b>665</b>
Pm	1080	1700	1500	720	1040	430	620	850	510	640
Sm	<b>1160</b>	<b>1669</b>	1450	820	<b>1040</b>	400	720	<b>857</b>	600	<b>640</b>
Eu	<b>1188</b>	<b>1584</b>	1290	<b>824</b>	<b>1062</b>	230	760	<b>799</b>	630	<b>540</b>
Gd	870	<b>1699</b>	1310	500	<b>937</b>	180	400	<b>829</b>	290	<b>619</b>
Tb	980	<b>1707</b>	<b>1742</b>	600	<b>1008</b>	600	500	850	390	<b>598</b>
Dy	1050	<b>1678</b>	1540	<b>693</b>	<b>1007</b>	420	590	<b>831</b>	470	<b>603</b>
Ho	1040	<b>1698</b>	1500	660	<b>990</b>	350	580	830	450	<b>594</b>
Er	1020	<b>1699</b>	1510	640	<b>995</b>	360	560	<b>836</b>	420	<b>586</b>
Tm	1090	<b>1689</b>	1500	<b>709</b>	<b>995</b>	360	640	840	500	<b>582</b>
Yb	<b>1172</b>	<b>1570</b>	1250	<b>799</b>	<b>960</b>	250	710	800	580	<b>561</b>
Lu	790	<b>1640</b>	1210	420	<b>986</b>	160	330	850	190	<b>556</b>

<sup>a</sup> Values are quoted as  $-\Delta H_f$  (kJ/mol).

Experimental values in bold.

Values taken from D.W. Smith, *J. Chem. Educ.*, 1986, **63**, 228.

LaF<sub>4</sub> might decompose thus :



Applying Hess's Law to this in the form

$$\Delta H_{\text{reaction}} = \sum \Delta H_f(\text{products}) - \sum \Delta H_f(\text{reactants})$$

$$\Delta H_{\text{reaction}} = -1732 - (-691 + 0) = -1041 \text{ kJ/mol}$$

This decomposition is thus thermodynamically favourable (especially as it would be favoured on entropy grounds too, with the formation of fluorine gas)

LaF<sub>2</sub> might decompose by disproportionation:



Using  $\Delta H_f$  for LaF<sub>2</sub> and for LaF<sub>3</sub> (–831 and –1732 kJ/mol respectively),  $\Delta H$  for this decomposition reaction can be calculated as –971 kJ/mol. This is again a very exothermic process, indicating that LaF<sub>2</sub> is likely to be unstable (this is analogous to the reason for the non-existence of MgCl, as disproportionation into Mg and MgCl<sub>2</sub> is favoured, as the reader may be aware). The reason for this is that, although  $I_3$  for lanthanum is large (and endothermic), it is more than compensated for by the higher lattice energy for LaF<sub>3</sub> compared with the value for LaF<sub>2</sub>.

Since both CeF<sub>3</sub> and CeF<sub>4</sub> are isolable, what makes the difference here? If similar calculations are carried out (assuming lattice energies for CeF<sub>3</sub> and CeF<sub>4</sub> of –4915 and –8391 kJ/mol respectively, and an enthalpy of atomization of 398 kJ/mol for Ce (see Table 2.6), and using the same enthalpy of atomization and electron affinity for fluorine as in the lanthanum examples),  $\Delta H_f$  for CeF<sub>3</sub> can be calculated as –1726 kJ/mol and  $\Delta H_f$  for CeF<sub>4</sub> as –1899 kJ/mol.

The discrepancy between  $\Delta H_f$  for CeF<sub>3</sub> and CeF<sub>4</sub> is much smaller than is the case for lanthanum. In fact, for the decomposition reaction



**Table 2.6** Enthalpies of atomization of the lanthanides (kJ/mol)

Ba	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf
150.9	402.1	398	357	328		164.8	176	301	391	293	303	280	247	159	428.0	570.7

$\Delta H = -1726 - (-1899) = +173$  kJ/mol, making the decomposition of  $\text{CeF}_4$  relatively unfavourable.  $\text{CeF}_4$  is stable, certainly at ambient temperatures.

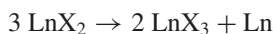
If the values of the parameters used in the calculation are compared, the determining factor is the much lower value of  $I_4$  for cerium (3547 kJ/mol compared with 4819 kJ/mol for La) due to the fact that the fourth electron is being removed from a different shell (nearer the nucleus) in the case of lanthanum.

Other tetrahalides do not exist. Thus, though both  $\text{CeCl}_3$  and salts of the  $[\text{CeCl}_6]^{2-}$  ion can be isolated,  $\text{CeCl}_4$  cannot be made. The reasons for this are those that enable fluorine to support high oxidation states (see Question 2.4). Similar factors indicate that tetrabromides and tetraiodides are much less likely to be isolated.

## 2.9.2 Stability of Dihalides

The stability of the dihalides can be explained in a similar way. As already noted,  $\text{LaF}_2$  does not exist. When might dihalides be expected?

One way in which dihalides can decompose is disproportionation



though a number of dihalides (particularly dichlorides) have been made by the reverse reproporationation, by heating the mixture to a high temperature and rapidly quenching (Section 3.5.1.)



It can be shown, using Hess's Law, that the disproportionation will be exothermic unless:

$$\Delta H_f \text{LnX}_3 / \Delta H_f \text{LnX}_2 < 1.5$$

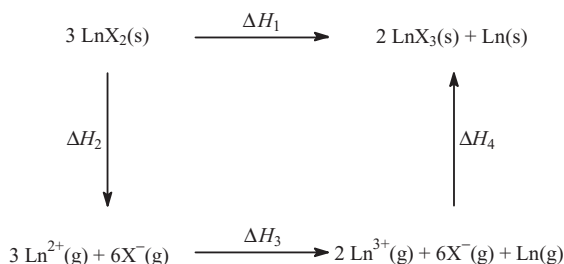
The disproportionation can be broken down into individual components (Figure 2.5)

$$\Delta H_1 = \Delta H_2 + \Delta H_3 + \Delta H_4$$

$$\Delta H_1 = [-3\Delta H_{\text{latt}}(\text{LnX}_2)] + \{2 I_3(\text{Ln}) - [I_1(\text{Ln}) + I_2(\text{Ln})]\}$$

$$+ [-\Delta H_{\text{at}}(\text{Ln}) + 2 \Delta H_{\text{latt}}(\text{LnX}_3)]$$

$$\Delta H_1 = \{2 I_3(\text{Ln}) - [I_1(\text{Ln}) + I_2(\text{Ln})]\} + 2 \Delta H_{\text{latt}}(\text{LnX}_3) - 3 \Delta H_{\text{latt}}(\text{LnX}_2) - \Delta H_{\text{at}}(\text{Ln})$$

**Figure 2.5**

Disproportion of lanthanide dihalides.

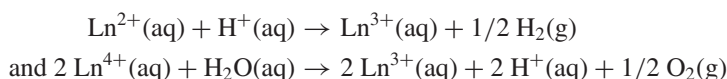
These equations can be used qualitatively, first to suggest for which lanthanides the halides  $\text{LnX}_2$  are most likely to be stable. For the disproportionation process to be more likely to be endothermic (i.e. stabilizing the +2 state), the preceding equation suggests that high values of  $I_3$  are favourable. Study of Table 2.2 shows that this is more likely to be associated with Eu, Sm and Yb. Iodide is the halide most often found in low oxidation state halides. In the case of  $\text{LnI}_2$ , the large size of the iodide ion will reduce the lattice energy for both  $\text{LnI}_2$  and  $\text{LnI}_3$  so that the *difference* in lattice enthalpy will become less significant, favouring  $\text{LnI}_2$ . The dihalide will also be favoured by a low  $\Delta H_{\text{at}}(\text{Ln})$ , again associated with the lanthanides most often found in the +2 state, Eu and Yb (see Table 2.6).

Applying the  $\Delta H_{\text{f}} \text{LnX}_3 / \Delta H_{\text{f}} \text{LnX}_2 < 1.5$  criterion, and using data in Table 2.5, the halides  $\text{LnX}_2$  are most likely to be stable are predicted to be  $\text{LnF}_2$  ( $\text{Ln} = \text{Sm}, \text{Eu}, \text{Yb}$ );  $\text{LnCl}_2$  ( $\text{Ln} = \text{Nd}, \text{Pm}, \text{Sm}, \text{Eu}, \text{Dy}, \text{Tm}, \text{Yb}$ );  $\text{LnY}_2$  ( $\text{Y} = \text{Br}, \text{I}; \text{Ln} = \text{Pr}, \text{Nd}, \text{Pm}, \text{Sm}, \text{Eu}, \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}, \text{Yb}$ ).

The known dihalides are listed in Table 3.2. There is a reasonably good correlation, given that the Pm dihalides have not been investigated on account of promethium's short half-life. Some dihalides listed are 'metallic' and are not covered by this argument.

### 2.9.3 Stability of Aqua Ions

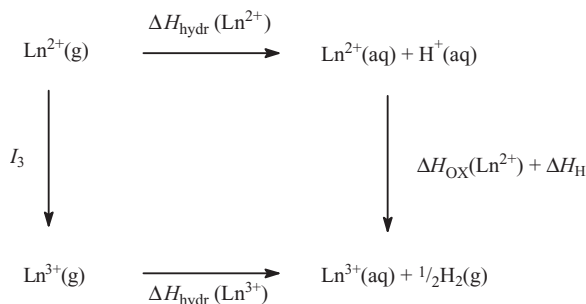
Since  $\text{Ln}^{3+}(\text{aq})$  is the most stable aqua ion, then both of the following processes are favoured.



In other words,  $\text{Ln}^{2+}$  ions tend to reduce water and  $\text{Ln}^{4+}$  ions tend to oxidize it. We can examine the stability of the  $\text{Ln}^{2+}$  ion using a treatment similar to the one just employed (Figure 2.6), with

$$\Delta H_{\text{ox}}(\text{Ln}^{2+}) = I_3 + \{[\Delta H_{\text{hydr}}[\text{Ln}^{3+}(\text{aq})] - \Delta H_{\text{hydr}}[\text{Ln}^{2+}(\text{aq})]]\} - 439 \text{ kJ/mol}.$$

When is it most likely that  $\text{Ln}^{2+}(\text{aq})$  ions will be stable? For the first of the two reactions above to be favoured, the single factor that will help make  $\Delta H$  positive is a high value of  $I_3$ . Less important would be the size of the ions, as this could affect the hydration enthalpies; the difference between the hydration enthalpies will be less, the larger the lanthanide ions. Substituting into the above equation, we can investigate the relative stabilities of  $\text{La}^{2+}(\text{aq})$  and  $\text{Eu}^{2+}(\text{aq})$ , making use of ionization energies from



**Figure 2.6**  
Oxidation of  $\text{Ln}^{2+}(\text{aq})$ .

Table 2.2 and enthalpies of hydration found in Table 2.4, also assuming  $\Delta H_{\text{hydr}} [\text{La}^{2+}(\text{aq})] = -1327 \text{ kJ/mol}$ :

For  $\text{La}^{2+}$ :

$$\begin{aligned}\Delta H_{\text{ox}}(\text{La}^{2+}) &= I_3 + \{\Delta H_{\text{hydr}}[\text{La}^{3+}(\text{aq})] - \Delta H_{\text{hydr}}[\text{La}^{2+}(\text{aq})]\} - 439 \\ &= 1850 + [-3278 - (-1327)] - 439 \\ &= -540 \text{ kJ/mol}\end{aligned}$$

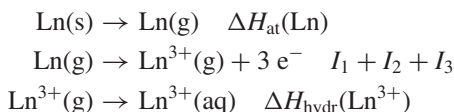
For  $\text{Eu}^{2+}$ :

$$\begin{aligned}\Delta H_{\text{ox}}(\text{Eu}^{2+}) &= I_3 + \{\Delta H_{\text{hydr}}[\text{Eu}^{3+}(\text{aq})] - \Delta H_{\text{hydr}}[\text{Eu}^{2+}(\text{aq})]\} - 439 \\ &= 2404 + [-3501 - (-1458)] - 439 \\ &= -78 \text{ kJ/mol}\end{aligned}$$

The large exothermic value for  $\Delta H_{\text{ox}}(\text{La}^{2+})$  indicates that it is not likely to exist in aqueous solution. The  $\text{Eu}^{2+}(\text{aq})$  ion is known to have a short lifetime in water, even though  $\Delta H$  is negative for the oxidation process, so the activation energy for oxidation may be rather high.

## 2.10 Patterns in Redox Potentials

Known and estimated values are listed in Table 2.7. The values for the reduction potential for  $\text{Ln}^{3+} + 3 \text{ e}^- \rightarrow \text{Ln}$  are very consistent, with slight irregularities at Eu and Yb. The potential largely depends upon three processes:



The first two of these are endothermic and the third exothermic; overall  $\Delta H$  is the difference between two large quantities. It remains fairly constant across the series, apart from Eu and Yb, with values of 608 (La); 712 (Eu); 630 (Gd); 613 (Tm); 644 (Yb) and 593 (Lu) kJ/mol being representative, the values for Eu and Yb resulting from the high  $I_3$  values. The very negative value for the reduction potential is expected for such reactive metals (and also reflects the difficulty in isolating them). The potentials for the  $\text{Ln}^{3+} + \text{e}^- \rightarrow \text{Ln}^{2+}$  process reflect the stability of the +2 state. Since  $I_3$  relates to  $\Delta H$  for the process, and  $\Delta G = -nFE$ , a relationship between these is unsurprising. Similarly, the only potential for the  $\text{Ln}^{4+} + \text{e}^- \rightarrow \text{Ln}^{3+}$  process within reasonable range is that for Ce, and indicates that  $\text{Ce}^{4+}$  is the only ion in this state likely to be encountered in aqueous solution.

**Question 2.1** What is the trend in atomic radii, and that in ionic radii, for the lanthanides? What are the exceptions to this, and why?

**Answer 2.1** The structure of metals is usually described as one in which metal ions are surrounded by a ‘sea’ of delocalised outer-shell electrons. The greater the number of loosely held electrons, the stronger the metallic bonding and the smaller the atomic radius. If the

**Table 2.7** Redox potentials of the lanthanide ions (V)<sup>a</sup>

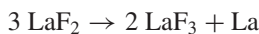
	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y
$\text{Ln}^{3+} + 3\text{e} \rightarrow \text{Ln}$	-2.37	-2.34	-2.35	-2.32	-2.29	-2.30	-1.99	-2.29	-2.30	-2.29	-2.33	-2.31	-2.31	-2.22	-2.30	-2.37
$\text{Ln}^{3+} + \text{e} \rightarrow \text{Ln}^{2+}$	(-3.1)	(-3.2)	(-2.7)	-2.6 <sup>b</sup>	(-2.6)	-1.55	-0.34	(-3.9)	(-3.7)	-2.5 <sup>b</sup>	(-2.9)	(-3.1)	-2.3 <sup>b</sup>	-1.05		
$\text{Ln}^{++} + \text{e} \rightarrow \text{Ln}^{3+}$		1.70	(3.4)	(4.6)	(4.9)	(5.2)	(6.4)	(7.9)	(3.3)	(5.0)	(6.2)	(6.1)	(6.1)	(7.1)	(8.5)	

<sup>a</sup>Values in parentheses are estimated.

<sup>b</sup> = in THF.

lanthanides are represented as  $\text{Ln}^{3+}(\text{e}^-)_3$ , then the atomic radii would be expected to fall between those of barium  $[\text{Ba}^{2+}(\text{e}^-)_2]$  and hafnium  $[\text{Hf}^{4+}(\text{e}^-)_4]$ , as is generally observed.

**Question 2.2** Using Hess's Law and the  $\Delta H_f$  for  $\text{LaF}_2$  ( $-831$  kJ/mol) and for  $\text{LaF}_3$  ( $-1732$  kJ/mol), calculate  $\Delta H$  for this decomposition reaction.



**Answer 2.2**

$$\begin{aligned}\Delta H_{\text{reaction}} &= \Sigma \Delta H_f(\text{products}) - \Sigma \Delta H_f(\text{reactants}) \\ \Delta H_{\text{reaction}} &= 2(-1732) - 3(-831 + 0) = -971 \text{ kJ/mol}\end{aligned}$$

**Question 2.3** Assuming lattice energies for  $\text{CeF}_3$  and  $\text{CeF}_4$  of  $-4915$  and  $-8391$  kJ/mol respectively, and using the same enthalpy of atomization and electron affinity for fluorine as in the lanthanum examples (Section 2.9.1.), calculate  $\Delta H_f$  for  $\text{CeF}_3$  and  $\text{CeF}_4$ . Take an enthalpy of atomization of  $398$  kJ/mol for cerium (Table 2.6). Use ionization energies from Table 2.2.

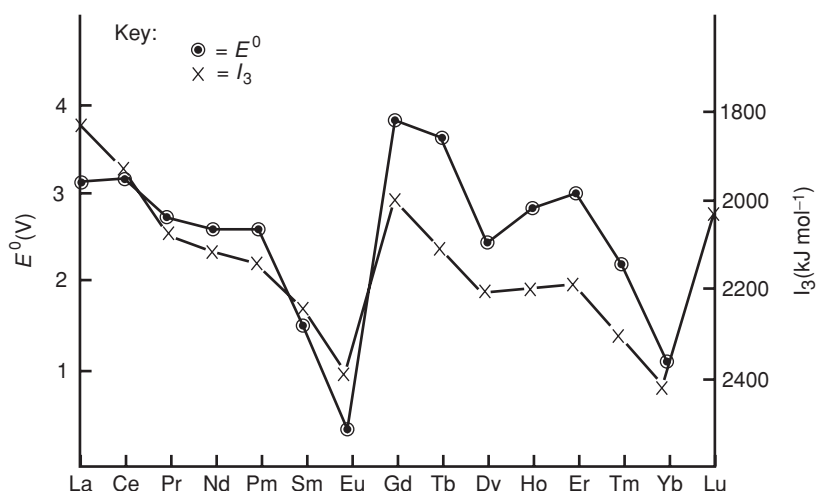
**Answer 2.3**

	$\Delta H(\text{kJ/mol})$
$\text{Ce(s)} \rightarrow \text{Ce(g)}$	+398
$\text{Ce(g)} \rightarrow \text{Ce}^{3+}(\text{g})$	+527 + 1047 + 1949
$3/2 \text{F}_2(\text{g}) \rightarrow 3\text{F}(\text{g})$	+252
$3\text{F}(\text{g}) + 3\text{e}^- \rightarrow 3\text{F}^-(\text{g})$	-984
$\text{Ce}^{3+}(\text{g}) + 3\text{F}^-(\text{g}) \rightarrow \text{CeF}_3(\text{s})$	-4915
Thus $\text{Ce(s)} + 3/2 \text{F}_2(\text{g}) \rightarrow \text{CeF}_3(\text{s})$	
$\Delta H = +398 + (527 + 1047 + 1949) + 252 - 984 - 4915 = -1726 \text{ kJ/mol}$	

	$\Delta H(\text{kJ/mol})$
$\text{Ce(s)} \rightarrow \text{Ce(g)}$	+398
$\text{Ce(g)} \rightarrow \text{Ce}^{4+}(\text{g})$	+527 + 1047 + 1949 + 3547
$2\text{F}_2(\text{g}) \rightarrow 4\text{F}(\text{g})$	+336
$4\text{F}(\text{g}) + 4\text{e}^- \rightarrow 4\text{F}^-(\text{g})$	-1312
$\text{Ce}^{4+}(\text{g}) + 4\text{F}^-(\text{g}) \rightarrow \text{CeF}_4(\text{s})$	-8391
Thus $\text{Ce(s)} + 2\text{F}_2(\text{g}) \rightarrow \text{CeF}_4(\text{s})$	
$\Delta H = +398 + (527 + 1047 + 1949 + 3547) + 336 - 1312 - 8391 = -1899 \text{ kJ/mol}$	

**Question 2.4** Unlike  $\text{CeF}_4$ ,  $\text{CeCl}_4$  does not exist, though  $\text{CeCl}_3$  does. Suggest why this might be. Values of  $\Delta H_f$  for  $\text{CeCl}_3$  and  $\text{CeCl}_4$  are  $-1058$  and  $-820$  (calculated) kJ/mol, respectively.

**Answer 2.4** Fluorine is well known to promote high oxidation states. Factors associated with this are the high lattice energies associated with the small fluoride ion, along with the very small F-F bond energy (due to non-bonding electron pair repulsions) as well as high bond energies involving fluorine (not relevant in this case). Because of the larger size of the  $\text{Cl}^-$  ion, there is going to be much less difference between the lattice energies of  $\text{CeCl}_3$  and

**Figure 2.7**

Strong correlation between  $I_3$  and  $E^\circ$  for  $\text{Ln}^{3+} + e \rightarrow \text{Ln}^{2+}$  (reproduced by permission of Macmillan from S.A. Cotton, *Lanthanides and Actinides*, 1991, p. 26.)

$\text{CeCl}_4$ , and this is probably the determining factor. The higher  $\Delta H_{\text{at}}(\text{Cl})$  of 121.5 kJ/mol also mitigates against the formation of  $\text{CeCl}_4$ .

**Question 2.5** Applying the  $\Delta H_f \text{LnX}_3 / \Delta H_f \text{LnX}_2 < 1.5$  criterion for stability of dihalides, and using data in Table 2.5, predict which the halides  $\text{LnX}_2$  are most likely to be exist.

**Answer 2.5** As in section 2.9.2  $\text{LnF}_2$  ( $\text{Ln} = \text{Sm}, \text{Eu}, \text{Yb}$ );  $\text{LnCl}_2$  ( $\text{Ln} = \text{Nd}, \text{Pm}, \text{Sm}, \text{Eu}, \text{Dy}, \text{Tm}, \text{Yb}$ );  $\text{LnY}_2$  ( $\text{Y} = \text{Br}, \text{I}$ ;  $\text{Ln} = \text{Pr}, \text{Nd}, \text{Pm}, \text{Sm}, \text{Eu}, \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}, \text{Yb}$ ) are predicted to be stable, in reasonably good agreement with the currently known facts.

**Exercise 2.6** Using the same horizontal axis (atomic numbers 57–71), plot values of (a) the third ionization enthalpy  $I_3$  and (b) the  $\text{Ln}^{3+} + e \rightarrow \text{Ln}^{2+}$  reduction potential on the y axis (choose appropriate scales). Comment.

**Answer 2.6** There is a strong correlation between them, not surprisingly! See Figure 2.7.

# 3 The Lanthanide Elements and Simple Binary Compounds

By the end of this chapter you should be able to:

- know how to prepare lanthanide metals and simple binary compounds such as the halides, oxides, and hydrides;
- apply the principle of the lanthanide contraction to explain patterns in co-ordination number in these compounds;
- apply knowledge gained in the study of Chapter 2 to the compounds in unusual oxidation states;
- understand the uses of the metals and certain compounds in applications such as hydrogen storage and in superconductors.

## 3.1 Introduction

This chapter discusses the synthesis of the lanthanide metals, their properties, reactions, and uses. It also examines some of the most important binary compounds of the lanthanides, particularly the halides, which well illustrate patterns and trends in the lanthanide series.

## 3.2 The Elements

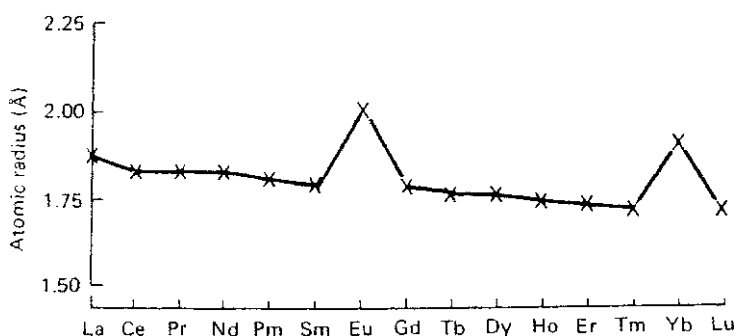
### 3.2.1 Properties

The lanthanides are rather soft reactive silvery solids with a metallic appearance, which tend to tarnish on exposure to air. They react slowly with cold water and rapidly in dilute acid. They ignite in oxygen at around 150–200 °C; similar reactions occur with the halogens, whilst they react on heating with many nonmetals such as hydrogen, sulfur, carbon, and nitrogen (above 1000 °C).

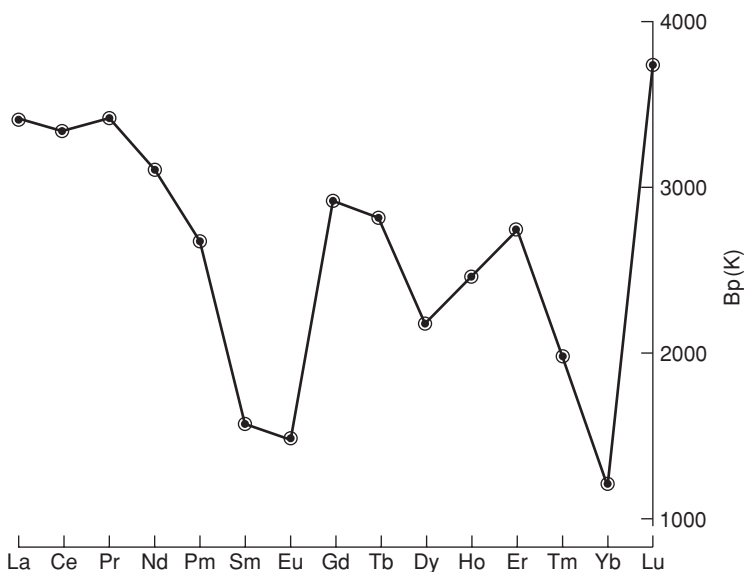
The metals are relatively high-melting and -boiling. Their physical properties usually show smooth transition across the series, except that discontinuities are often observed for the metals that have a stable +2 state, europium and ytterbium. Thus the atomic radii of europium and ytterbium are about 0.2 Å greater than might be predicted by interpolation from values for the flanking lanthanides (Figure 3.1).

Similarly, Sm, Eu, and Yb have boiling points that are lower than those of the neighbouring metals (Figure 3.2).



**Figure 3.1**

The atomic radii of the lanthanide metals (reproduced with permission from S.A. Cotton, *Lanthanides and Actinides*, Macmillan, 1991).

**Figure 3.2**

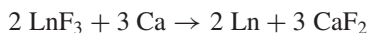
The boiling points of the lanthanide metals (reproduced with permission from S.A. Cotton, *Lanthanides and Actinides*, Macmillan, 1991).

Assuming that one can represent the structure of a metal as a lattice of metal ions permeated by a sea of electrons, then metals like lanthanum can be shown as  $(\text{Ln}^{3+})(\text{e}^{-})_3$ ; however, metals based upon divalent ions (like Eu and Yb) would be  $(\text{Ln}^{2+})(\text{e}^{-})_2$ . The ions with the (+3) charge have a smaller radius, as the higher charge draws in the electrons more closely, and the stronger attraction means that it takes more energy to boil them (similarly, they would be predicted to have higher conductivities).

### 3.2.2 Synthesis

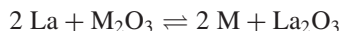
The metals have similar reactivities to magnesium. This means that they cannot be extracted by methods like carbon reduction of the oxides; in practice, metallothermic reduction of the lanthanide fluoride or chloride with calcium at around 1450 °C is used. The product

is an alloy of (excess of) calcium and the lanthanide, from which the calcium can be distilled.



The reduction is carried out under an atmosphere of argon, not nitrogen.

The above method is not suitable for obtaining the metals with a stable +2 state, which are only reduced as far as the difluoride (Eu, Yb, Sm). The lanthanide can be removed by distillation.



The ‘divalent’ metals Sm, Eu, and Yb have boiling points of 1791, 1597 and 1193 °C respectively, much lower than that of La (3457 °C), so that on heating they are distilled off, their volatility meaning that their removal from the mixture will displace the equilibrium to the right, so the reaction will proceed to completion.

### 3.2.3 Alloys and Uses of the Metals

Mischmetal is the lanthanide alloy with the longest history. It is a mixture of the lighter lanthanides, cerium in particular, which is manufactured from an ‘unseparated’ mixture of the oxides. This is first converted into a mixture of the anhydrous chlorides, which is then electrolysed using a graphite anode and iron cathode at around 820 °C to afford the mixture of metals. This is used mainly as an alloy with iron for the desulfurization and deoxidation of steels and more familiarly in cigarette lighter flints.  $\text{SmCo}_5$  and other alloys of these metals have been used to make extremely strong permanent magnets.  $\text{LaNi}_5$  has been widely examined as a material for hydrogen storage, with applications in fuel cells, catalytic hydrogenation, and removal of hydrogen from gas mixtures, as it rapidly absorbs hydrogen at room temperature to afford compositions up to  $\text{LaNi}_5\text{H}_6$ ; the hydrogen is given up quickly at 140 °C. The most important application lies in rechargeable batteries for PCs (see Section 3.10).

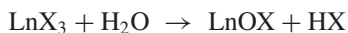
## 3.3 Binary Compounds

### 3.3.1 Trihalides

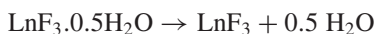
Most halides are  $\text{LnX}_3$ , but a number of  $\text{LnX}_2$  are known, as are a handful of tetrafluorides.

#### *Syntheses of the Trihalides*

Although the halides can be obtained as hydrates from reaction of the metal oxides or carbonates with aqueous acids, these hydrates are hydrolysed on heating to the oxyhalide and thus the anhydrous halides (which are themselves deliquescent) cannot be made that way.



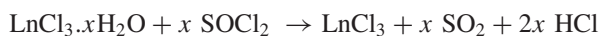
The fluorides are obtained as insoluble hydrates  $\text{LnF}_3 \cdot 0.5\text{H}_2\text{O}$  by precipitation and the hydrates dehydrated by heating in a current of anhydrous HF gas (or *in vacuo*).



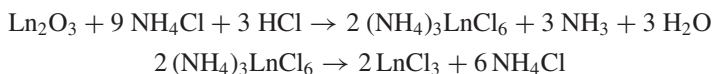
Otherwise the anhydrous halides can generally be made by heating the metal with the halogen (except for  $\text{EuI}_3$ ) or gaseous  $\text{HCl}$ .



Another method for the chlorides involves refluxing the hydrated chlorides with thionyl dichloride ( $\text{SOCl}_2$ ) for a few hours; an advantage of this method is that the other reaction products are gaseous  $\text{SO}_2$  and  $\text{HCl}$ .



A route that works well in practice involves thermal decomposition of ammonium halogenometallates. Adding ammonium chloride to a solution of the metal oxides in hydrochloric acid, followed by evaporation gives halogenometallate salts. These can be dehydrated by heating with excess of ammonium chloride in a stream of gaseous  $\text{HCl}$ , the resulting anhydrous salt being decomposed by heating *in vacuo* at about  $300^\circ\text{C}$ .



The anhydrous halides can be purified by sublimation *in vacuo*, but owing to a tendency to react with silica, contact with hot glass, thereby forming the oxyhalide, should be avoided.

### Structures of the Trihalides

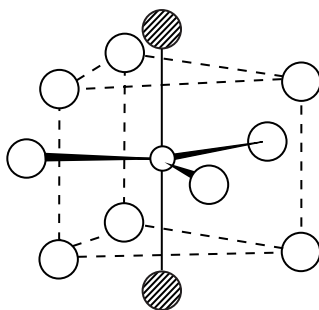
The lanthanide trihalides demonstrate very clearly the effect of varying the cation and anion radii upon the structure type adopted (Table 3.1).

The early lanthanide fluorides adopt the ‘ $\text{LaF}_3$ ’ structure (Figure 3.3) based on a metal ion surrounded by a trigonal prism of fluorides with two additional capping fluorides, giving 11 coordination ( $9 + 2$ ), whilst the later fluorides have the ‘ $\text{YF}_3$ ’ structure. This is based on tricapped trigonal prismatic 9 coordination, in which the prism is somewhat distorted. The structure adopted by  $\text{UCl}_3$  and several of the lanthanide halides is again a tricapped

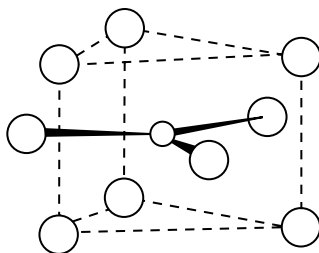
**Table 3.1** Structures of the lanthanide trihalides

	F	Cl	Br	I
La	$\text{LaF}_3$ (11)	$\text{UCl}_3$ (9)	$\text{UCl}_3$ (9)	$\text{PuBr}_3$ (8)
Ce	$\text{LaF}_3$ (11)	$\text{UCl}_3$ (9)	$\text{UCl}_3$ (9)	$\text{PuBr}_3$ (8)
Pr	$\text{LaF}_3$ (11)	$\text{UCl}_3$ (9)	$\text{UCl}_3$ (9)	$\text{PuBr}_3$ (8)
Nd	$\text{LaF}_3$ (11)	$\text{UCl}_3$ (9)	$\text{PuBr}_3$ (8)	$\text{PuBr}_3$ (8)
Pm	$\text{LaF}_3$ (11)	$\text{UCl}_3$ (9)	$\text{PuBr}_3$ (8)	$\text{PuBr}_3$ (8)
Sm	$\text{YF}_3$ (9)	$\text{UCl}_3$ (9)	$\text{PuBr}_3$ (8)	$\text{FeCl}_3$ (6)
Eu	$\text{YF}_3$ (9)	$\text{UCl}_3$ (9)	$\text{PuBr}_3$ (8)	
Gd	$\text{YF}_3$ (9)	$\text{UCl}_3$ (9)	$\text{FeCl}_3$ (6)	$\text{FeCl}_3$ (6)
Tb	$\text{YF}_3$ (9)	$\text{PuBr}_3$ (8)	$\text{FeCl}_3$ (6)	$\text{FeCl}_3$ (6)
Dy	$\text{YF}_3$ (9)	$\text{AlCl}_3$ (6)	$\text{FeCl}_3$ (6)	$\text{FeCl}_3$ (6)
Ho	$\text{YF}_3$ (9)	$\text{AlCl}_3$ (6)	$\text{FeCl}_3$ (6)	$\text{FeCl}_3$ (6)
Er	$\text{YF}_3$ (9)	$\text{AlCl}_3$ (6)	$\text{FeCl}_3$ (6)	$\text{FeCl}_3$ (6)
Tm	$\text{YF}_3$ (9)	$\text{AlCl}_3$ (6)	$\text{FeCl}_3$ (6)	$\text{FeCl}_3$ (6)
Yb	$\text{YF}_3$ (9)	$\text{AlCl}_3$ (6)	$\text{FeCl}_3$ (6)	$\text{FeCl}_3$ (6)
Lu	$\text{YF}_3$ (9)	$\text{AlCl}_3$ (6)	$\text{FeCl}_3$ (6)	$\text{FeCl}_3$ (6)
Y	$\text{YF}_3$ (9)	$\text{AlCl}_3$ (6)	$\text{FeCl}_3$ (6)	$\text{FeCl}_3$ (6)

Values in parentheses indicate the coordination number.

**Figure 3.3**

The  $\text{LaF}_3$  structure (reproduced by permission of Macmillan from S.A. Cotton, *Lanthanides and Actinides*, 1991, p. 42).

**Figure 3.4**

The structure of  $\text{UCl}_3$  and certain  $\text{LnCl}_3$  [reproduced in modified form, from R.B. King (ed.), *Encyclopedia of Inorganic Chemistry*, 1st edition, Wiley, Chichester; 1994].

trigonal prism (Figure 3.4); if one of the face-capping halogens is removed from the ‘ $\text{UCl}_3$ ’ structure, the 8 coordinate  $\text{PuBr}_3$  structure is generated. Finally, the  $\text{AlCl}_3$  and  $\text{BiI}_3$  (also sometimes referred to as ‘ $\text{FeCl}_3$ ’) structures both have octahedral six-coordination.

The trends are similar to those found in halides of the Group I and Group II metals and are explained on an ionic packing model; more anions can be packed round the large lanthanide ions early in the series than around the smaller, later ones; similarly, more of the small fluoride ions can be packed round a given lanthanide ion than is the case with the much larger iodide anion.

### *Properties of the Trihalides*

The trihalides are high-melting solids, with many uses in synthetic chemistry, though their insolubility in some organic solvents means that complexes, such as those with thf (Section 4.3.3), are often preferred.

### **3.3.2 Tetrahalides**

Only the fluorides of Ce, Pr, and Tb exist, the three lanthanides with the most stable (+4) oxidation state. Fluorine is most likely to support a high oxidation state, and even though salts of ions like  $[\text{CeCl}_6]^{2-}$  are known, the binary chloride has not been made.  $\text{CeF}_4$  can be crystallized from aqueous solution as a monohydrate. Anhydrous  $\text{LnF}_4$  ( $\text{Ln} = \text{Ce, Pr, Tb}$ )

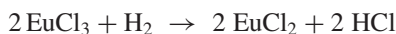
can be made by fluorination of the trifluoride or, in the case of Ce, by fluorination of metallic Ce or  $\text{CeCl}_3$ . All three tetrafluorides have the  $\text{MF}_4$  structure with dodecahedral eight coordination. Factors that favour formation of a tetrafluoride include a low value of  $I_4$  for the metal and a high lattice energy (see Section 2.9.1). This is most likely to be found with the smallest halide ion, fluoride. The low bond energy of  $\text{F}_2$  is also a supporting factor.

### 3.3.3 Dihalides

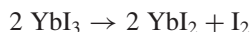
These are most common for metals with a stable (+2) state, such as Eu, Yb, and Sm. As would be expected, they most often occur for the iodide ion, the best reducing agent. A number of dihalides are known for other metals, though some of these do not actually involve the (+2) oxidation state.

#### Synthetic Routes

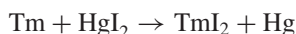
These compounds are usually made by reduction using hydrogen (e.g.  $\text{EuX}_2$ ,  $\text{YbX}_2$ , or  $\text{SmI}_2$ ) or reproporationation.



In a few cases, thermal decomposition is applicable [ $\text{LnI}_2$  ( $\text{Ln} = \text{Sm}, \text{Yb}$ );  $\text{EuBr}_2$ ].



Another method, used especially for diiodides, involves heating the metal with  $\text{HgX}_2$ .



The known dihalides are listed in Table 3.2, together with an indication of the structure and coordination number.

The iodides of Nd, Sm, Eu, Dy, Tm, and Yb are definitely compounds of the +2 ions, with salt-like properties, are insulators, and have magnetic and spectroscopic properties expected

**Table 3.2** Structures of the lanthanide dihalides

	F	Cl	Br	I
La				<sup>a</sup> $\text{MoSi}_2$ (8)
Ce				<sup>a</sup> $\text{MoSi}_2$ (8)
Pr				<sup>a</sup> $\text{MoSi}_2$ (8)
Nd		$\text{PbCl}_2$ (9)	$\text{PbCl}_2$ (9)	$\text{SrBr}_2$ (7,8)
Pm				
Sm	$\text{CaF}_2$ (8)	$\text{PbCl}_2$ (9)	$\text{PbCl}_2$ (9); $\text{SrBr}_2$ (7,8)	$\text{EuI}_2$ (7)
Eu	$\text{CaF}_2$ (8)	$\text{PbCl}_2$ (9)	$\text{SrBr}_2$ (7,8)	$\text{EuI}_2$ (7)
Gd				<sup>a</sup> $\text{MoSi}_2$ (8)
Tb				
Dy		$\text{SrBr}_2$ (7,8)	$\text{SrI}_2$ (7)	$\text{CdCl}_2$ (6)
Ho				
Er				
Tm		$\text{SrI}_2$ (7)	$\text{SrI}_2$ (7)	$\text{CdI}_2$ (6)
Yb	$\text{CaF}_2$ (8)	$\text{SrI}_2$ (7)	$\text{SrI}_2$ (7); $\text{CaCl}_2$ (6)	$\text{CdI}_2$ (6)
Lu				

<sup>a</sup>  $\text{Ln}^{\text{III}}$  compounds with the structure  $\text{M}^{3+}(\text{I}^-)_2(\text{e}^-)$ .

for the  $M^{2+}$  ions (thus electronic spectra of  $\text{EuX}_2$  resemble those of the isoelectronic  $\text{Gd}^{3+}$  ions).  $\text{SmI}_2$  is proving an important reagent in synthetic organic chemistry (Section 8.3).

Several of the diiodides, however, have a metallic sheen and are very good conductors of electricity, such as  $\text{LaI}_2$ ,  $\text{CeI}_2$ ,  $\text{PrI}_2$ , and  $\text{GdI}_2$ . Since they are good conductors in the solid state, the presence of delocalized electrons is indicated.  $M^{3+}(\text{I}^-)_2(\text{e}^-)$  is a likely structure. None of these metals exhibits a stable +2 state in any of its compounds and consideration of factors such as their ionization energies suggest they are unlikely to form stable compounds in this state (see Section 2.9.2).

### 3.3.4 Oxides

#### *Oxides $M_2O_3$*

As already mentioned, the metals burn easily, rather like Group 2 metals, forming oxides (but with some nitride). The oxides are therefore best made by thermal decomposition of compounds like the nitrate or carbonate.



Most lanthanides form  $\text{Ln}_2\text{O}_3$ , but those metals with accessible +4 and +2 oxidation states can afford other stoichiometries. These may be turned into  $\text{Ln}_2\text{O}_3$  by synthesis under a reducing atmosphere.  $\text{CeO}_2$  can be reduced to  $\text{Ce}_2\text{O}_3$  using hydrogen. The oxides are somewhat basic and absorb  $\text{CO}_2$  from the atmosphere, forming carbonates, and water vapour, forming hydroxides. As expected they dissolve in acid, forming salts, and are convenient starting materials for the synthesis of lanthanide salts, including the hydrated halides.

The sesquioxides  $\text{Ln}_2\text{O}_3$  adopt three structures, depending upon the temperature and upon the lanthanide involved. At room temperature,  $\text{La}_2\text{O}_3$  to  $\text{Sm}_2\text{O}_3$  inclusive adopt the A-type structure, which has capped octahedral 7 coordination of the lanthanide. The B-type structure tends to be exhibited by  $\text{La}_2\text{O}_3$  to  $\text{Sm}_2\text{O}_3$  at higher temperatures and has three different lanthanide sites, one with distorted 6 coordination and the others with face-capped octahedral 7 coordination. The C-type structure is followed by heavier metals and has 6 coordination, severely distorted from an octahedron.

#### *Oxides $\text{MO}_2$*

Cerium, having the stablest (+4) state, is the only metal to form a stoichiometric oxide in this state,  $\text{CeO}_2$ , which has the fluorite structure. It is white when pure, but even slightly impure specimens tend to be yellow. It can be made by burning cerium or heating salts like cerium(III) nitrate strongly in air. It is basic and dissolves with some difficulty in acid, forming  $\text{Ce}^{4+}(\text{aq})$ , which can be isolated as salts such as the nitrate  $\text{Ce}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ . Uses of  $\text{CeO}_2$  include self-cleaning ovens and as an oxidation catalyst in catalytic converters.

Praseodymium and terbium form higher oxides, of which a number of phases are known between  $\text{Ln}_2\text{O}_3$  and  $\text{LnO}_2$ . Ignition of praseodymium nitrate leads to  $\text{Pr}_2\text{O}_3$  but further heating in an oxygen atmosphere gives  $\text{Pr}_6\text{O}_{11}$  or even  $\text{PrO}_2$ ; terbium similarly yields  $\text{Tb}_4\text{O}_7$  and  $\text{TbO}_2$ .

#### *Oxides $\text{MO}$*

Reduction of  $\text{Eu}_2\text{O}_3$  with Eu above 800 °C (comproportionation) gives  $\text{EuO}$ .

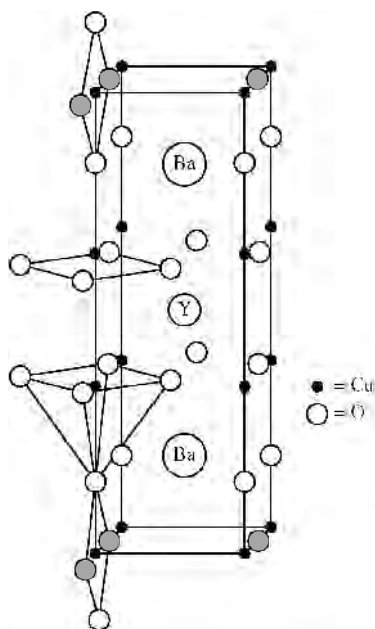


This compound and the similar YbO have salt-like (NaCl) structures and are genuine  $\text{Ln}^{\text{II}}$  compounds, being insulators. Similar comproportionation methods using high pressures have been used to obtain SmO and NdO; these are shiny conducting solids, probably containing  $\text{Ln}^{3+}$  ions.

### Oxide Superconductors

Superconductivity is the phenomenon in which a material conducts electricity with virtually zero resistance. For many years until the mid 1980s, the highest temperatures available were around 20 K and required expensive liquid helium (or hydrogen) coolant. If high-temperature superconductors can be made, this has obvious application in area such as power transmission. In 1986, Bednorz and Muller reported that  $\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_4$  was a superconductor up to 38 K. This sparked intense world-wide activity, and the following year Wu, Chu and others reported that  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  ( $0 \leq \delta \leq 1$ ) had a  $T_c$  (superconducting transition temperature) of 92 K, bringing the phenomenon into the liquid nitrogen range. Steady though less spectacular advances have produced materials like  $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_8$  ( $T_c = 133\text{K}$ ).

The structure of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  is based on an oxygen-deficient layered perovskite structure and features two types of copper environment (Figure. 3.5), formally containing  $\text{Cu}^{2+}$  and  $\text{Cu}^{3+}$ , with both square planar and square pyramidal coordination. Removing the shaded oxygens results in phases down to the semiconductor  $\text{YBa}_2\text{Cu}_3\text{O}_6$ . The mechanism of superconductivity is still debated, but one theory suggests that it involves an electron passing through the lattice distorting it in such a way that a second electron follows closely in its wake



**Figure 3.5**

The structure of  $\text{YBa}_2\text{Cu}_3\text{O}_7$ ; the shaded atoms are those removed to create oxygen-deficient phases up to  $\text{YBa}_2\text{Cu}_3\text{O}_6$  (reproduced by permission of Macmillan from S.A. Cotton, *Lanthanides and Actinides*, 1991, p. 47).

with no hindrance to its passing, the electron pair being known as a 'Cooper pair'. Despite intense activity over the last 15 years no truly commercial material has yet emerged, due to the intrinsically brittle nature of the oxide ceramic materials making fabrication into wires impossible. Current thinking favours making thin films, though with present technology they will only have low current-carrying capacity.

### 3.4 Borides

A number of stoichiometries obtain, such as  $\text{LnB}_2$ ,  $\text{LnB}_4$ ,  $\text{LnB}_6$ ,  $\text{LnB}_{12}$ , and  $\text{LnB}_{66}$ .

The most important are  $\text{LnB}_6$ . Borides are obtained by heating the elements together at 2000 °C or by heating the lanthanide oxide with boron or boron carbide at 1800 °C. They are extremely unreactive towards acids, alkalis, and other chemicals, and are metallic conductors. They contain a continuous three-dimensional framework of  $(\text{B}_6)^{2-}$  octahedra interspersed with  $\text{Ln}^{3+}$  ions, indicating an electronic structure  $(\text{Ln}^{3+})(\text{B}_6)^{2-}(\text{e}^-)$  in most cases, though  $\text{EuB}_6$  and  $\text{YbB}_6$  are insulators, suggesting them to be  $(\text{Ln}^{2+})(\text{B}_6)^{2-}$ . Because of its high thermal stability and melting point (2400 °C), and its metal-like electrical and thermal conductivity,  $\text{LaB}_6$  is an important thermionic emitter material for the cathodes of electron guns. Mixed boride materials are also of commercial importance. Nd–Fe–B alloys, with compositions such as  $\text{Nd}_2\text{Fe}_{14}\text{B}$ , are the strongest permanent magnet materials available today. Other important compounds include lanthanide rhodium boride low-temperature superconductors (such as  $\text{ErRh}_4\text{B}_4$ ), part of a wider  $\text{LnM}_4\text{B}_4$  family ( $\text{M}$  = transition metal).

### 3.5 Carbides

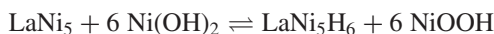
The lanthanides form carbides with a range of compositions, notably  $\text{LnC}_2$ , but additionally  $\text{Ln}_2\text{C}_3$ ,  $\text{LnC}$ ,  $\text{Ln}_2\text{C}$ , and  $\text{Ln}_3\text{C}$  phases are known (depending upon the lanthanide in question and the conditions of synthesis).  $\text{LnC}_2$  adopt the  $\text{CaC}_2$  structure, containing isolated  $\text{C}_2^{2-}$  ions.

### 3.6 Nitrides

These can be made by direct synthesis from the elements at 1000 °C. They have the NaCl structure and can be hydrolysed to  $\text{NH}_3$ .

### 3.7 Hydrides

Ternary hydrides such as  $\text{LaNi}_5\text{H}_6$  have attracted attention as materials for electrodes in fuel cells and for gas storage. Nickel/metal hydride batteries for notebook PCs are a less toxic alternative than Ni/Cd batteries; when charging, hydrogen generated at the negative electrode enters the lattice of the La/Ni alloy (in practice a material such as  $\text{La}_{0.8}\text{Nd}_{0.2}\text{Ni}_{2.5}\text{Co}_{2.4}\text{Si}_{0.1}$  is used to improve corrosion resistance, storage capacity, discharge rate, etc.). The overall cell reaction is:





The lanthanides also form simple binary hydrides on combination of the elements at about 300 °C. These compounds have ideal compositions of  $\text{MH}_2$  and  $\text{MH}_3$ , but are frequently non-stoichiometric. Thus lutetium forms phases with ranges  $\text{LuH}_{1.83}$  to  $\text{LuH}_{2.23}$  and  $\text{LuH}_{2.78}$  to  $\text{LuH}_{3.00}$ . Reaction of ytterbium with hydrogen under pressure gives  $\text{YbH}_{2.67}$ .  $\text{MH}_3$  are obtained only at higher gas pressures, whilst europium, the lanthanide with the most stable +2 state, forms only  $\text{EuH}_2$ . The dihydrides are generally good electrical conductors, and thus are thought to be  $\text{M}^{3+}(\text{H}^-)_2(\text{e}^-)$ , whilst the trihydrides are salt-like nonconductors believed to be  $\text{M}^{3+}(\text{H}^-)_3$ . The hydrides are reactive solids, owing to the presence of the easily hydrolysed  $\text{H}^-$  ion.

### 3.8 Sulfides

These are quite important compounds. A number of stoichiometries exist, the most important being  $\text{Ln}_2\text{S}_3$ . These can be made by direct synthesis, heating the elements together, or by passing  $\text{H}_2\text{S}$  over heated  $\text{LnCl}_3$ .  $\text{Eu}_2\text{S}_3$  cannot be prepared by this latter route.

A range of compositions between  $\text{Ln}_2\text{S}_3$  and  $\text{Ln}_3\text{S}_4$ , the latter formed when  $\text{Ln}_2\text{S}_3$  lose sulfur on heating, generally occurs.  $\text{Ln}_2\text{S}_3$  are insulators, genuine  $\text{Ln}(\text{III})$  compounds, but  $\text{Ln}_3\text{S}_4$  (having the  $\text{Th}_3\text{P}_4$  structure) are more complex. Some, like  $\text{Ce}_3\text{S}_4$ , are metallic conductors and are thus  $(\text{Ln}^{3+})_3(\text{S}^{2-})_4(\text{e}^-)$ ; others, like  $\text{Eu}_3\text{S}_4$  and  $\text{Sm}_3\text{S}_4$ , are semiconductors and may be  $(\text{Ln}^{2+})(\text{Ln}^{3+})_2(\text{S}^{2-})_4$ . The structures of  $\text{Ln}_2\text{S}_3$  fall into a pattern.  $\text{La}_2\text{S}_3$  to  $\text{Dy}_2\text{S}_3$  adopt the ‘ $\text{Gd}_2\text{S}_3$ ’ structure with 7-coordinate lanthanide ions;  $\text{Dy}_2\text{S}_3$  to  $\text{Tm}_2\text{S}_3$  have the ‘ $\text{Ho}_2\text{S}_3$ ’ structure with 6- and 7-coordinate lanthanides, whilst  $\text{Yb}_2\text{S}_3$  and  $\text{Lu}_2\text{S}_3$  have the corundum structure with just 6 coordination.

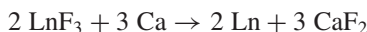
Monsulfides  $\text{MS}$  are formed by direct combination. They adopt the  $\text{NaCl}$  structure but have a variety of bonding types.  $\text{YbS}$  and  $\text{EuS}$  are genuine  $\text{Ln}^{2+} \text{S}^{2-}$  but  $\text{CeS}$  exhibits the magnetic properties expected for  $\text{Ce}^{3+}$  and has a bronze metallic lustre as well, so it thought to be  $(\text{Ce}^{3+})(\text{S}^{2-})(\text{e}^-)$ . This substance not only has electrical conductivity in the metallic region but also can be machined like a metal too.  $\text{SmS}$  has some unusual properties; it is usually obtained as a black semiconducting phase,  $\text{Sm}^{2+} \text{S}^{2-}$ , but can reportedly be turned into a golden metallic phase by the action of pressure, polishing or even scratching on single crystals.

Oxysulfides are also rather important.  $\text{Y}_2\text{O}_2\text{S}$  is used as a host material for  $\text{Ln}^{3+}$  ion emitters (e.g.  $\text{Eu}$ ,  $\text{Tb}$ ) in some phosphors, notably those used in TV screens. When mischmetal is used to remove oxygen and sulfur from impure iron and steel, the product is an oxysulfide, which forms an immiscible solid even in contact with molten steel and thus does not contaminate the product.

**Question 3.1.** Why do  $\text{Eu}$  and  $\text{Yb}$  have lower boiling points than the other lanthanides and significantly higher atomic radii?

**Answer 3.1** Most lanthanides can be described by an electronic structure  $(\text{Ln}^{3+})(\text{e}^-)_3$ , whereas metals like  $\text{Eu}$  and  $\text{Yb}$  can be better described by  $(\text{Ln}^{2+})(\text{e}^-)_2$ . The greater charge on the (+3) ions draws electrons in closer, so it is expected that the metals with this electronic structure will have smaller atoms. Similarly the greater number of electrons in the  $(\text{Ln}^{3+})(\text{e}^-)_3$  structure leads to stronger metallic bonding than in metals with the structure  $(\text{Ln}^{2+})(\text{e}^-)_2$  and hence the weaker cohesive force requires less energy to overcome it, resulting in lower enthalpies of vapourization and lower boiling points.

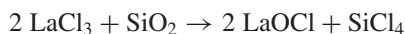
**Question 3.2** Suggest why nitrogen is not a suitable inert atmosphere for the following reaction:



**Answer 3.2** Like magnesium, which forms  $\text{Mg}_3\text{N}_2$ , hot lanthanides react with nitrogen, forming the nitride  $\text{LnN}$  (see Section 3.9).

**Question 3.3** Produce a balanced equation for the reaction of  $\text{LaCl}_3$  with silica.

**Answer 3.3**



**Question 3.4** Studying the data in Table 3.1 if necessary, explain the patterns in coordination number of the lanthanide trihalides.

**Answer 3.4** As the radius of the lanthanide ion decreases on crossing the series from left to right, the coordination number of the metal in a given halide decreases; a similar effect is seen on descending Group 7(17), as the radius of the halide ion increases.

**Question 3.5** The melting and boiling points of  $\text{LaX}_3$  ( $X = \text{Cl}, \text{Br}, \text{I}$ ) are 862/1750 °C ( $X = \text{Cl}$ ); 789 and 1580 °C ( $X = \text{Br}$ ); 778 and 1405 °C ( $X = \text{I}$ ). Comment on these values.

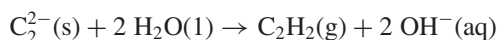
**Answer 3.5** The melting point is an indication of the magnitude of the lattice energy, whilst the boiling point is a measure of the attraction between the mobile ions. Lattice energy decreases as the size of the anions increase, so it would be least for the iodide. Covalent character in the bonding, which would also decrease the melting point, increases in the same direction.

**Question 3.6** Why could  $\text{CeO}_2$  be a useful catalyst for oxidations?

**Answer 3.6** As with  $\text{V}_2\text{O}_5$  in the Contact process for making sulfuric acid, the ability of cerium to adopt transition-metal-like behaviour in switching oxidation states means that the cerium oxide can effectively act as an oxygen-storage system.

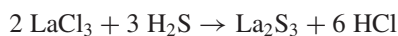
**Question 3.7**  $\text{LnC}_2$  are good conductors of electricity and form ethyne,  $\text{C}_2\text{H}_2$ , on hydrolysis (as does  $\text{CaC}_2$ , traditionally used in ‘acetylene’ headlamps on early cars and bicycles). Explain these observations.

**Answer 3.7** These compounds have the structure  $\text{M}^{3+}(\text{C}_2^{2-})(\text{e}^-)$ . The delocalized electrons cause the high conductivity. The ethynide ions react with water thus:



**Question 3.8** Suggest an equation for the reaction of  $\text{LaCl}_3$  with  $\text{H}_2\text{S}$ .

**Answer 3.8**





# 4 Coordination Chemistry of the Lanthanides

By the end of this chapter you should be able to:

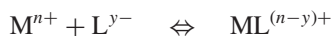
- recall which donor atoms and types of ligand form the most stable complexes;
- explain why later lanthanides form complexes with greater stability constants than do the earlier lanthanides;
- explain why polydentate ligands form more stable complexes;
- recall and explain the most common coordination numbers in lanthanide complexes;
- recall the common geometries of complexes;
- work out coordination numbers and suggest geometries of complexes, given a formula;
- explain the choice of particular compounds as Magnetic Resonance Imaging agents.

## 4.1 Introduction

Forty years ago, very little was known about lanthanide complexes. By analogy with the d-block metals, it was often assumed that lanthanides were generally six coordinate in their complexes. We now know that this is not the case, that lanthanides (and actinides) show a wider variety of coordination number than do the d-block metals, and also understand the reasons for their preferred choice of ligand.

## 4.2 Stability of Complexes

For the reaction between a metal ion and a ligand



a stability constant may be defined approximately

$$\beta_1 = [ML^{(n-y)+}] / [M^{n+}][L^{y-}]$$

Table 4.1 lists  $\log[\beta_1]$  values for  $La^{3+}$  and  $Lu^{3+}$  as well as  $Sc^{3+}$  and  $Y^{3+}$  with a number of common ligands, whilst Table 4.2 gives the  $\log[\beta_1]$  values for all the lanthanide ions complexing with  $EDTA^{4-}$ ,  $DTPA^{5-}$ , and fluoride.

The values for  $Lu^{3+}$  are greater than those for  $La^{3+}$  as the smaller  $Lu^{3+}$  ion has a greater charge density and stronger electrostatic attraction for a ligand. The stability constants for the smaller halide ligands are greater on account of their higher charge density. Values for multidentate ligands are greater because of entropy factors (see below) and also because

**Table 4.1** Aqueous stability constants ( $\log \beta_1$ ) for lanthanide (3+) and other ions

Ligand	I (mol/dm <sup>3</sup> )	La <sup>3+</sup>	Lu <sup>3+</sup>	Y <sup>3+</sup>	Sc <sup>3+</sup>	Fe <sup>3+</sup>	Cu <sup>2+</sup>	Ca <sup>2+</sup>	U <sup>4+</sup>	UO <sub>2</sub> <sup>2+</sup>	Th <sup>4+</sup>
F <sup>-</sup>	1.0	2.67	3.61	3.60	6.2 <sup>a</sup>	5.2	0.9	0.6	7.78	4.54	7.46
Cl <sup>-</sup>	1.0	-0.1	-0.4	-0.1	0	0.63	-0.06	-0.11	0.30	-0.10	0.18
Br <sup>-</sup>	1.0	-0.2		-0.15	-0.07	-0.2	-0.5		0.2	-0.3	-0.13
NO <sub>3</sub> <sup>-</sup>	1.0	0.1	-0.2		0.3	-0.5	-0.01	-0.06	0.3	-0.3	0.67 <sup>a</sup>
OH <sup>-</sup>	0.5	4.7	5.8	5.4	9.0	11.27	6.3 <sup>a</sup>	1.0	12.2	8.0 <sup>a</sup>	9.6 <sup>a</sup>
acac <sup>-</sup>	0.1	4.94	6.15	5.89	8	10	8.16				8
EDTA <sup>4-</sup>	0.1	15.46	19.8	18.1	23.1	25.0	18.7	10.6	25.7	7.4	25.3
DTPA <sup>5-</sup>	0.1	19.5	22.4	22.4	24.4	28	21.4	10.8			28.8
OAc <sup>-</sup>	0.1	1.82	1.85	1.68		3.38	1.83	0.5 <sup>a</sup>		2.61	3.89
glycine	0.1	3.1	3.9	3.5		10.0 <sup>a</sup>	8.12	1.05			

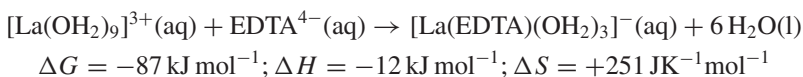
<sup>a</sup> = Data for solutions of slightly different ionic strength**Table 4.2** Aqueous stability constants ( $\log \beta_1$ ) for lanthanide (3+) ions with fluoride, EDTA, and DTPA

Ligand	Y <sup>3+</sup>	La <sup>3+</sup>	Ce <sup>3+</sup>	Pr <sup>3+</sup>	Nd <sup>3+</sup>	Pm <sup>3+</sup>	Sm <sup>3+</sup>	Eu <sup>3+</sup>	Gd <sup>3+</sup>	Tb <sup>3+</sup>	Dy <sup>3+</sup>	Ho <sup>3+</sup>	Er <sup>3+</sup>	Tm <sup>3+</sup>	Yb <sup>3+</sup>	Lu <sup>3+</sup>
F <sup>-</sup>	3.60	2.67	2.87	3.01	3.09	3.16	3.12	3.19	3.31	3.42	3.46	3.52	3.54	3.56	3.58	3.61
EDTA <sup>4-</sup>	18.08	15.46	15.94	16.36	16.56		17.10	17.32	17.35	17.92	18.28	18.60	18.83	19.30	19.48	19.80
DTPA <sup>5-</sup>	22.05	19.48	20.33	21.07	21.60		22.34	22.39	22.46	22.71	22.82	22.78	22.74	22.72	22.62	22.44

once one end of a ligand is attached, there is a higher chance of the other donor atoms attaching themselves (conversely, with a multidentate ligand, if a bond to one donor atom is broken, the others hold).

In a graph of  $\log K$  against  $Z$  (the atomic number), there is a smooth increase expected as the ionic radius decreases as the greater charge density of the smaller ions leads to more stable complexes. There are inflections, particularly around Gd, possibly due to the change in coordination number of the aqua ion.

For these complexation reactions,  $\Delta H$  has small values, either exothermic or endothermic; the main driving force for complex formation, particularly where multidentate ligands are involved, is the large positive entropy change. Thus for:



In the reaction



where L = 2,6-dipicolinate and X is bromate or ethyl sulfate, there is a smooth variation in  $\Delta H$  across the series, as there is no change in the coordination number of the aqua ion.

In general, lanthanide ions prefer to bind to hard donors such as O and F, rather than to soft bases such as P and S donor ligands. Nitrogen-containing ligands are an apparent anomaly, since they form relatively few complexes; this is at least partly due to the high basicity of such ligands, tending to result in the precipitation of hydroxides, etc. (Lanthanide amines have been made in solvents like supercritical NH<sub>3</sub>.) The higher electronegativity of oxygen and consequent polar nature of ligands like phosphine oxides R<sub>3</sub>P<sup>δ+</sup>=O<sup>δ-</sup> is also a factor. Use of nonaqueous solvents of weak donor ability (e.g. MeCN) can lead to the isolation of complexes decomposed by water.

## 4.3 Complexes

### 4.3.1 The Aqua Ions

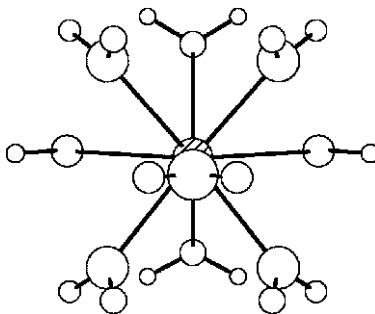
The coordination number of  $[\text{Ln}(\text{H}_2\text{O})_n]^{3+}$  is believed to be 9 for the early lanthanides (La–Eu) and 8 for the later metals (Dy–Lu), with the intermediate metals exhibiting a mixture of species. The nine-coordinate species are assigned tricapped trigonal prismatic structures (Figure 4.1) and the eight-coordinate species square antiprismatic coordination. A considerable amount of spectroscopic data has led to this conclusion; for example, the visible spectrum of  $\text{Nd}^{3+}(\text{aq})$  and  $[\text{Nd}(\text{H}_2\text{O})_9]^{3+}$  ions in solid neodymium bromate are very similar to each other and quite different to those of  $\text{Nd}^{3+}$  ions in eight-coordinate environments, correlating with solution X-ray and neutron-diffraction studies, indicating  $n \sim 8.9$  in solution. Similarly, neutron-diffraction studies indicate  $n \sim 8.5$  for  $\text{Sm}^{3+}(\text{aq})$  and 7.9 for  $\text{Dy}^{3+}(\text{aq})$  and  $\text{Lu}^{3+}(\text{aq})$ , whilst solution luminescence studies suggest  $n$  values of 9.0, 9.1, 8.3, and 8.4 for  $\text{Sm}^{3+}$ ,  $\text{Eu}^{3+}$ ,  $\text{Tb}^{3+}(\text{aq})$ , and  $\text{Dy}^{3+}$  respectively.

### 4.3.2 Hydrated Salts

These are readily prepared by reaction of the lanthanide oxide or carbonate with the acid. Salts of noncoordinating anions most often crystallize as salts  $[\text{Ln}(\text{OH}_2)_9]\text{X}_3$  (X e.g. bromate, triflate, ethyl sulfate, tosylate). These contain the  $[\text{Ln}(\text{OH}_2)_9]^{3+}$  ion (Figure 4.1), even for the later lanthanides, where in aqueous solution the eight-coordinate species  $[\text{Ln}(\text{OH}_2)_8]^{3+}$  predominates.

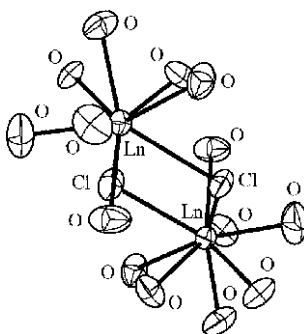
The lanthanide–water distances for the positions capping the prism faces and at the vertices are different; on crossing the series from La to Lu, the Ln–O distance decreases from 2.62 to 2.50 Å for the three face-capping oxygens but change more steeply from 2.52 to 2.29 Å for the six apical oxygens (data for the triflate). In contrast, the perchlorate salts are  $[\text{Ln}(\text{OH}_2)_6](\text{ClO}_4)_3$  and eight-coordinate species are found in species like  $[\text{Er}(\text{OH}_2)_8](\text{ClO}_4)_3 \cdot (\text{dioxane}) \cdot 2\text{H}_2\text{O}$ ,  $[\text{Eu}(\text{OH}_2)_8]_2(\text{V}_{10}\text{O}_{28}) \cdot 8\text{H}_2\text{O}$ , and as  $[\text{Gd}(\text{OH}_2)_8]^{3+}$  ions encapsulated inside a crown ether ring. Many of these compounds have lattices held together by hydrogen bonds, a factor which clearly affects the solubility and hence the compound isolated.

When anions can coordinate, a wide variety of species obtains. Some examples follow. Among the nitrates,  $[\text{Ln}(\text{NO}_3)_3 \cdot (\text{H}_2\text{O})_5]$  (Ln = La, Ce) have 11-coordinate lanthanides



**Figure 4.1**

The structure of the nonaqua lanthanide ion (reproduced by permission of the American Chemical Society from B.P. Hay, *Inorg. Chem.*, 1991, **30**, 2881).

**Figure 4.2**

Structure of the dimeric cation  $[(\text{H}_2\text{O})_7\text{LnCl}_2\text{Ln}(\text{H}_2\text{O})_7]^{4+}$  (reproduced by permission of the International Union of Crystallography from A. Habenschuss and F.H. Spedding, *Cryst. Struct. Commun.*, 1982, 7, 538).

whilst in  $[\text{Ln}(\text{NO}_3)_3 \cdot (\text{H}_2\text{O})_4]$  ( $\text{Ln} = \text{Pr} - \text{Yb}$ , Y) 10 coordination is the rule, and two hydrates containing 9-coordinate  $[\text{Lu}(\text{NO}_3)_3 \cdot (\text{H}_2\text{O})_3]$  species have been characterized; in general, in lanthanide complexes a coordinated nitrate group is *almost always* bidentate. The chlorides and bromides of La and Ce,  $\text{LnX}_3 \cdot 7\text{H}_2\text{O}$ , are dimeric  $[(\text{H}_2\text{O})_7\text{Ln}(\mu\text{-X})_2\text{Ln}(\text{OH}_2)_7]\text{X}_4$  ( $\text{X} = \text{Cl}, \text{Br}$ ; Figure 4.2), whilst  $\text{LnCl}_3 \cdot 6\text{H}_2\text{O}$  ( $\text{Ln} = \text{Nd} - \text{Lu}$ ) have antiprismatic  $[\text{LnCl}_2(\text{OH}_2)_6]^+$  ions.

Amongst the hydrated bromides,  $\text{LnBr}_3 \cdot 6\text{H}_2\text{O}$  ( $\text{Ln} = \text{Pr} - \text{Dy}$ ) are  $[\text{LnBr}_2(\text{OH}_2)_6]\text{Br}$ , like the heavier rare earth chlorides; and  $\text{LnBr}_3 \cdot 8\text{H}_2\text{O}$  ( $\text{Ln} = \text{Ho} - \text{Lu}$ ) are  $[\text{Ln}(\text{OH}_2)_8]\text{Br}_3$ . The structures of the iodides  $\text{LnI}_3 \cdot 9\text{H}_2\text{O}$  and  $\text{LnI}_3 \cdot 8\text{H}_2\text{O}$  also involve pure aqua ions. Several hydrated sulfates exist, where both water and sulfates are bound to the metal, usually with 9 coordination. Thiocyanates exist as  $\text{Ln}(\text{NCS})_3(\text{H}_2\text{O})_6$  ( $\text{Ln} = \text{La} - \text{Dy}$ ) and  $\text{Ln}(\text{NCS})_3(\text{H}_2\text{O})_5$  ( $\text{Ln} = \text{Sm} - \text{Eu}$ ) molecules.

The acetates, unlike the acetates of transition metals like  $\text{Cr}^{\text{III}}$ ,  $\text{Fe}^{\text{III}}$ , and  $\text{Ru}^{\text{III}}$ , do not adopt oxo-centred structures with  $\text{M}_3\text{O}$  cores. Instead,  $[\text{Ln}(\text{OAc})_3 \cdot 1.5(\text{H}_2\text{O})]$  ( $\text{Ln} = \text{La} - \text{Pr}$ ) have structures with acetate-bridged chains crosslinked by further acetate bridges;  $[\text{Ln}(\text{OAc})_3 \cdot (\text{H}_2\text{O})]$  ( $\text{Ln} = \text{Ce} - \text{Pr}$ ) have one-dimensional polymeric structures with acetate bridges; and  $[\text{Ln}(\text{OAc})_3 \cdot 4\text{H}_2\text{O}]$  ( $\text{Ln} = \text{Sm} - \text{Lu}$ ) are acetate-bridged dimers.

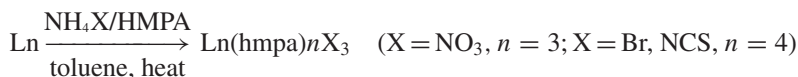
Adding oxalate ions to a solution of lanthanide ions affords quantitative precipitation of the oxalate; this is used in traditional quantitative analysis of lanthanides, as on ignition they are converted into the oxide, the weighing form.

The chloride, bromide, bromate, perchlorate, nitrate, acetate, and iodide salts are all soluble in water, the sulfates sparingly soluble, and the fluorides, carbonates, oxalates, and phosphates insoluble.

### 4.3.3 Other O-Donors

Complexes of lanthanide salts with neutral donors are generally made by mixing solutions of the ligand and the metal salt dissolved in a nonaqueous solvent such as ethanol or acetonitrile. Complexes of ligands like phosphine and arsine oxides were the first complexes of this type to be studied in detail. The best defined series involve hexamethylphosphoramide [hmpa:  $(\text{Me}_2\text{N})_3\text{PO}$ ] as a ligand; two series are obtained in which the stoichiometry is maintained across the series,  $\text{Ln}(\text{hmpa})_6(\text{ClO}_4)_3$  and  $\text{Ln}(\text{hmpa})_3\text{Cl}_3$ , with structural confirmation for

[Nd(hmpa)<sub>6</sub>](ClO<sub>4</sub>)<sub>3</sub> and *mer*-Ln(hmpa)<sub>3</sub>Cl<sub>3</sub> (Ln = Pr, Dy, Yb). Apart from the usual synthesis involving the ligand and the appropriate metal salt in ethanol, such complexes can also be made by an unusual ‘one-pot’ synthesis leading to the isolation of 9-coordinate La(hmpa)<sub>3</sub>(NO<sub>3</sub>)<sub>3</sub>, 7-coordinate La(hmpa)<sub>4</sub>(NCS)<sub>3</sub> and La(hmpa)<sub>4</sub>Br<sub>3</sub>.



Complexes of Ph<sub>3</sub>PO and Ph<sub>3</sub>AsO, though well known, have yet to be fully studied. The bulky phenyl groups exert at-a-distance steric effects, yet allow several ligands of this type to coordinate to a metal ion, as in [La(Ph<sub>3</sub>PO)<sub>5</sub>Cl] (FeCl<sub>4</sub>)<sub>2</sub> and [Ln(Ph<sub>3</sub>PO)<sub>4</sub>Cl<sub>2</sub>] (CuCl<sub>3</sub>), both of which have six-coordinate lanthanides. Early lanthanides form Ln(Ph<sub>3</sub>PO)<sub>4</sub>(NO<sub>3</sub>)<sub>3</sub> (La–Nd), which have two bidentate and one monodentate nitrates, giving 9-coordinate lanthanides; Lu(Ph<sub>3</sub>PO)<sub>4</sub>(NO<sub>3</sub>)<sub>3</sub> is actually [Ln(Ph<sub>3</sub>PO)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub>] NO<sub>3</sub>, with 8 coordination. Nine coordination is also known to occur in Eu(Ph<sub>3</sub>AsO)<sub>3</sub>(NO<sub>3</sub>)<sub>3</sub>. On the other hand, with a less bulky ligand, lanthanum attains 10 coordination in La(Ph<sub>2</sub>MePO)<sub>4</sub>(NO<sub>3</sub>)<sub>3</sub>. ‘Solvent’ is coordinated in Ln(Ph<sub>3</sub>PO)<sub>2</sub>(NO<sub>3</sub>)<sub>3</sub>(EtOH) (Ln = Ce–Eu), also 9-coordinate. Triflates Ln(Ph<sub>3</sub>PO)<sub>4</sub>(OTf)<sub>3</sub> (OTf = CF<sub>3</sub>SO<sub>3</sub>) contain [Ln(Ph<sub>3</sub>PO)<sub>4</sub>(OTf)<sub>2</sub>]<sup>+</sup> ions; for La and Nd, one triflate is bidentate and one monodentate, whilst for Er–Lu both triflates are monodentate. A few halide complexes have been characterized structurally, notably for Y, including [Y(Me<sub>3</sub>PO)<sub>6</sub>] Br<sub>3</sub> and [Y(Ph<sub>3</sub>PO)<sub>4</sub>Cl<sub>2</sub>] Cl, though it would be expected that lanthanide complexes would be analogous.

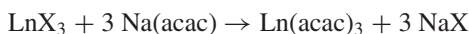
Complexes of tetrahydrofuran (thf) have been studied in considerable detail in recent years. The anhydrous metal chlorides, widely used in synthesis, are relatively insoluble in organic solvents whilst the ease of replacement of the labile thf molecules in the relatively soluble thf complexes makes them more useful synthetic reagents. Several types of complex have been characterized, including [LaCl<sub>3</sub>(thf)<sub>4</sub>] (seven coordinate); LnCl<sub>3</sub>(thf)<sub>3.5</sub>, actually [LnCl<sub>2</sub>(thf)<sub>5</sub>]<sup>+</sup> [LnCl<sub>4</sub>(thf)<sub>2</sub>]<sup>−</sup>, containing both seven- and six-coordinate lanthanides (formed by metals such as Sm and Eu); and octahedral [LnCl<sub>3</sub>(thf)<sub>3</sub>], only found for Yb and Lu (see Question 4.3, below).

Other complexes to have been studied include Nd(thf)<sub>4</sub>Br<sub>3</sub> and Yb(thf)<sub>4</sub>(NCS)<sub>3</sub>, both pentagonal bipyramidal seven-coordinate molecules with two axial halides (generally adopted for LnL<sub>4</sub>X<sub>3</sub> systems). The thiocyanate complexes of the earlier lanthanides, [Ln(thf)<sub>4</sub>(NCS)<sub>3</sub>]<sub>2</sub>, are dimers with two bridging thiocyanates affording eight coordination. Nitrate complexes Pr(thf)<sub>4</sub>(NO<sub>3</sub>)<sub>3</sub> and Yb(thf)<sub>3</sub>(NO<sub>3</sub>)<sub>3</sub> have been characterized, as recently have the iodides LnI<sub>3</sub>(THF)<sub>4</sub> [Ln = Pr] and LnI<sub>3</sub>(THF)<sub>3.5</sub> [Ln = Nd, Gd, Y], the latter being [LnI<sub>2</sub>(THF)<sub>5</sub>][LnI<sub>4</sub>(THF)<sub>2</sub>], analogous to some of the chlorides.

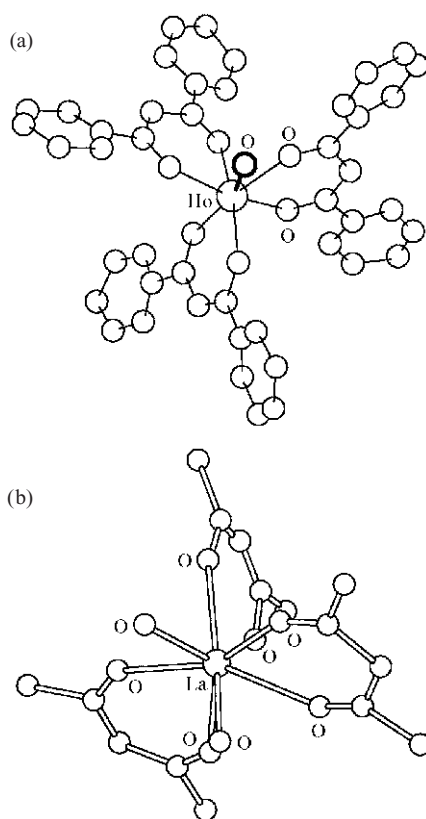
Another example of the lanthanide contraction at work, verified by crystallographers, lies in the complexes of the lanthanide nitrates with dimethyl sulfoxide (dmsO). The early lanthanides form 10-coordinate Ln(dmsO)<sub>4</sub>(NO<sub>3</sub>)<sub>3</sub> (Ln = La–Sm), whilst the heavier metals form Ln(dmsO)<sub>3</sub>(NO<sub>3</sub>)<sub>3</sub> (Ln = Eu–Lu, Y).

#### 4.3.4 Complexes of β-Diketonates

These are an important class of compounds with a general formula Ln(R<sup>1</sup>.CO.CH.CO.R<sup>2</sup>)<sub>3</sub>. The acetylacetonates, Ln(acac)<sub>3</sub> (R<sup>1</sup> = R<sup>2</sup> = CH<sub>3</sub>) can readily be made from a lanthanide salt and acetylactone by adding sodium hydroxide:





**Figure 4.3**

(a) The structure of  $\text{Ho}(\text{PhCOCHCOPh})_3(\text{H}_2\text{O})$  (reproduced by permission of the American Chemical Society from A. Zalkin, D.H. Templeton, and D.G. Karraker, *Inorg. Chem.*, 1969, **8**, 2680). (b) The structure of  $\text{La}(\text{acac})_3(\text{H}_2\text{O})_2$  (reproduced by permission of the American Chemical Society from T. Phillips, D.E. Sands, and W.F. Wagner, *Inorg. Chem.*, 1968, **7**, 2299).

They crystallize as hydrates  $\text{Ln}(\text{acac})_3 \cdot (\text{H}_2\text{O})_2$  ( $\text{Ln} = \text{La} - \text{Ho}, \text{Y}$ ) and  $\text{Ln}(\text{acac})_3 \cdot (\text{H}_2\text{O})$  ( $\text{Ln}$  e.g.  $\text{Yb}$ ) though there is a tendency to contain lattice water as well (Figure 4.3 for acac and  $\text{PhCOCHCOPh}$  complexes). These compounds are difficult to dehydrate, even *in vacuo*; they decompose on heating, and on dehydration at room temperature tend to oligomerize to involatile materials. They form Lewis base adducts like  $\text{Ln}(\text{acac})_3 \cdot (\text{Ph}_3\text{PO})$  and  $\text{Ln}(\text{acac})_3 \cdot (\text{phen})$  (7- and 8-coordinate, respectively).

Using bulkier R groups ( $\text{R}^1 = \text{R}^2 = \text{CMe}_3$ , for example) affords more congested diketone complexes that are more tractable;  $\text{Ln}(\text{Me}_3\text{CO.CH.CO.CMe}_3)_3$  [often abbreviated to  $\text{Ln}(\text{dpm})_3$  or  $\text{Ln}(\text{tmhd})_3$ ] are monomers in solution and sublime *in vacuo* at 100–200 °C; in the solid state they are dimers for  $\text{Ln} = \text{La} - \text{Dy}$  (CN 7) and monomers for  $\text{Dy} - \text{Lu}$  (CN 6) and have trigonal prismatic coordination. They tend to hydrate readily, forming adducts [e.g. capped trigonal prismatic  $\text{Ln}(\text{dpm})_3(\text{H}_2\text{O})$ ].

Complexes of fluorinated diketones ( $\text{R}^1 = \text{CF}_3$ ,  $\text{R}^2 = \text{CH}_3$ ,  $\text{L} = \text{tfac}$ ;  $\text{R}^1 = \text{R}^2 = \text{CF}_3$ ,  $\text{L} = \text{hfac}$ ;  $\text{R}^1 = \text{cyclo-C}_4\text{H}_3\text{S}$ ,  $\text{R}^2 = \text{CF}_3$ ,  $\text{L} = \text{tta}$ ;  $\text{R}^1 = \text{CF}_3\text{CF}_2\text{CF}_2$ ,  $\text{R}^2 = \text{CMe}_3$ ,  $\text{L} = \text{fod}$ ) are also important. Again, the initial complexes obtained in synthesis are hydrates that can be dehydrated *in vacuo*. 2-Thenoyltrifluoroacetone complexes  $\text{Ln}(\text{tta})_3 \cdot 2\text{H}_2\text{O}$  are important in

solvent extraction; addition of phosphine oxides gives a synergistic improvement in extraction owing to the formation of phosphine oxide complexes. Phosphine oxide complexes of hfac,  $\text{Ln}(\text{hfac})_3(\text{Bu}_3\text{PO})_2$ , can be separated by gas chromatography.

### 4.3.5 Lewis Base Adducts of $\beta$ -Diketonate Complexes

Because the diketonates  $\text{Ln}(\text{R}^1\text{CO.CH.CO.R}^2)_3$  are co-ordinatively unsaturated, they complete their coordination sphere by forming adducts with Lewis bases, as already noted. Because of the paramagnetism of nearly all of the lanthanide ions, there are resulting shifts in the resonances in the NMR spectrum of any organic molecule coordinated and this means that these complexes were formerly important as NMR Shift Reagents (see Section 5.5.1). Their stoichiometry and structure was consequently well researched. Both 1:1 and 1:2 adducts are possible, depending on steric factors of both the complex and the ligand. Solubility factors may also mean that the most abundant species in a solution is not that which crystallizes.  $\text{Ln}(\text{fod})_3$  forms both 1:1 and 1:2 complexes with even quite bulky bases (e.g. 2,4,6- $\text{Me}_3\text{py}$ ). In contrast, the more bulky  $\text{Eu}(\text{dpm})_3$  forms solid  $\text{Eu}(\text{dpm})_3\text{L}_2$  adducts with both pyridine and  $\text{C}_3\text{H}_7\text{NH}_2$ , but only  $\text{Eu}(\text{dpm})_3\text{L}$  with the bulkier 2-methylpyridine. Detailed studies of  $\text{Ho}(\text{dpm})_3$  have shown evidence only for 1:1 complexes with sterically demanding ligands like  $\text{Ph}_3\text{PO}$ , camphor, and borneol.

The structures are known for a number of these compounds; thus, of the eight-coordinate compounds,  $\text{Eu}(\text{acac})_3(\text{phen})$  is square antiprismatic,  $\text{Eu}(\text{dpm})_3(\text{py})_2$  and  $\text{Nd}(\text{tta})_3(\text{Ph}_3\text{PO})_2$  are dodecahedral; seven-coordinate  $\text{Lu}(\text{dpm})_3(3\text{-picoline})$  is a face-capped trigonal prism and  $\text{Eu}(\text{dpm})_3(\text{quinuclidine})$  a capped octahedron. Nine-coordination is found in  $\text{Eu}(\text{dpm})_3(\text{terpy})$  and also in  $\text{Pr}(\text{facam})_3(\text{DMF})_3$  (facam = 3-trifluoroacetyl-D-camphorate).

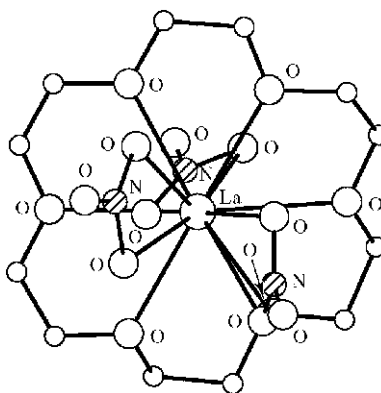
Anionic species of the type  $[\text{Ln}(\text{R}^1\text{CO.CH.CO.R}^2)_4]^-$  are another means of attaining coordinative saturation and are well known, such as the antiprismatic  $[\text{Eu}(\text{Ph.CO.CH.CO.Ph})_4]^-$  ion.

### 4.3.6 Nitrate Complexes

These exhibit high coordination numbers. Double nitrates  $\text{Mg}_3\text{Ln}_2(\text{NO}_3)_{12}\cdot 24\text{H}_2\text{O}$ , which contain  $[\text{Ln}(\text{NO}_3)_6]^{3-}$  ions, are important historically as they were once used for the separation of the lanthanides by fractional crystallization. Use of counter-ions like  $\text{Ph}_4\text{P}^+$  and  $\text{Me}_4\text{N}^+$  allow isolation of the 10-coordinate  $[\text{Ln}(\text{NO}_3)_5]^{2-}$  ions.

### 4.3.7 Crown Ether Complexes

In contrast to the alkali metals, the lanthanides do not form crown ether complexes readily in aqueous solution, due to the considerable hydration energy of the  $\text{Ln}^{3+}$  ion. These complexes are, however, readily synthesized by operating in non-aqueous solvents. Because many studies have been made with lanthanide nitrate complexes, coordination numbers are often high. Thus 12-coordination is found in  $\text{La}(\text{NO}_3)_3(18\text{-crown-6})$  (Figure 4.4), 11 coordination in  $\text{La}(\text{NO}_3)_3(15\text{-crown-5})$ , and 10 coordination is found in  $\text{La}(\text{NO}_3)_3(12\text{-crown-4})$ . Other complexes isolated include  $\text{Nd}(18\text{-crown-6})_{0.75}(\text{NO}_3)_3$ , which is in fact  $[\{\text{Nd}(18\text{-crown-6})(\text{NO}_3)_2\}^+]_3 [\text{Nd}(\text{NO}_3)_6]$ . Other lanthanide salts complex with crown ethers; small crowns like 12-crown-4 give 2:1 complexes with lanthanide perchlorates, though the 2:1 complexes are not obtained with lanthanide nitrates where the anion can

**Figure 4.4**

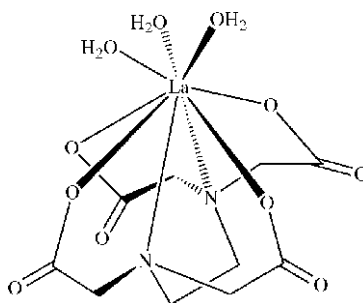
The structure of  $\text{La}(\text{NO}_3)_3 \cdot (18\text{-crown-6})$  (reproduced by permission of the Royal Society of Chemistry from J.D.J. Backer-Dirks, J.E. Cooke, A.M.R. Galas, J.S. Ghotra, C.J. Gray, F.A. Hart, and M.B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1980, 2191).

readily coordinate. Lanthanide chloride complexes often include water in the co-ordination sphere; thus the complex with the formula  $\text{ErCl}_3 \cdot (12\text{-crown-4}) \cdot 5\text{H}_2\text{O}$  actually contains 9-coordinate  $[\text{Er}(12\text{-crown-4})(\text{H}_2\text{O})_5]^{3+}$  cations whilst  $\text{NdCl}_3 \cdot (18\text{-crown-6}) \cdot 4\text{H}_2\text{O}$  is  $[\text{Nd}(18\text{-crown-6})\text{Cl}_2(\text{H}_2\text{O})_2]^+(\text{Cl}^-) \cdot 2\text{H}_2\text{O}$ . On reaction in MeCN/MeOH, 15-crown-5 reacts with neodymium chloride to form complexes with  $[\text{Nd}(\text{OH}_2)_9]^{3+}$  and  $[\text{NdCl}_2(\text{OH}_2)_6]^+$  ions hydrogen-bonded to the crown ether without any direct Nd–crown ether bonds. By carrying out electrocrystallization, the water-free  $[\text{Nd}(15\text{-crown-5})\text{Cl}_3]$  is obtained. Lanthanides also complex with the noncyclic linear polyethers such as glyme and with other macrocycles such as the calixarenes.

### 4.3.8 Complexes of EDTA and Related Ligands

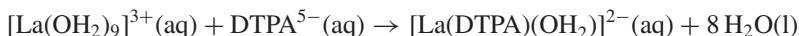
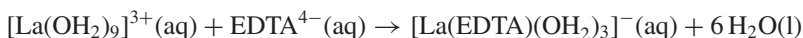
These complexes are not only interesting on account of their chemical and structural properties, but they have an important place in the history of lanthanide separation chemistry. Although lanthanide ions do not form strong complexes with N-donor ligands, EDTA and other polyaminopolycarboxylic acids also have a number of carboxylate groups that also coordinate to the  $\text{Ln}^{3+}$  ion. Early experiments on separating lanthanides were carried out on a tracer scale using citrate complexes, but EDTA and related ligands were found to give lanthanide complexes that afforded better separations on a large scale (Section 1.5); thus  $\log K$  for the EDTA complexes of  $\text{Pr}^{3+}$  and  $\text{Nd}^{3+}$  are 16.40 and 16.61, respectively; the average difference in  $K$  between adjacent lanthanides is  $10^{0.4}$ . EDTA is a hexadentate ligand; since transition metals can also coordinate a water molecule to form complexes like  $[\text{Fe}(\text{EDTA})(\text{H}_2\text{O})]^-$ , it is not surprising that lanthanides form complexes with more water molecules bound. The stoichiometry of the complex isolated depends to some extent upon the counter-ion; for example, nine-coordinate  $[\text{Ho}(\text{EDTA})(\text{H}_2\text{O})_3]^-$  ions are found in the crystal when  $M = \text{K}$ , whilst eight-coordinate  $[\text{Ho}(\text{EDTA})(\text{H}_2\text{O})_2]^-$  ions are found when  $M = \text{Cs}$ . In general, the early lanthanides form  $M[\text{Ln}(\text{EDTA})(\text{H}_2\text{O})_3]$  and the later ones  $[\text{M}(\text{EDTA})(\text{H}_2\text{O})_2]$ . {See Figure 4.5 for the  $[\text{La}(\text{EDTA})(\text{H}_2\text{O})_3]^-$  complex.}

Diethylenetriaminepentaacetic acid ( $\text{H}_5\text{DTPA}$ ) is a potentially octadentate ligand (realized in practice) and forms complexes with larger stability constants, of the type  $[\text{M}(\text{DTPA})(\text{H}_2\text{O})]^{2-}$ . DTPA complexes have greater stability constants than do EDTA

**Figure 4.5**

The structure of  $\text{La}(\text{EDTA})(\text{H}_2\text{O})_3^-$  (reproduced by permission of Macmillan from S.A. Cotton, *Lanthanides and Actinides*, 1991, p. 64).

complexes, since the greater denticity of the ligand makes it harder for the metal ion to be removed. Another factor is that the entropy change on complex formation is likely to be greater, thus making  $\Delta G$  (and hence  $K$ ) greater. Compare



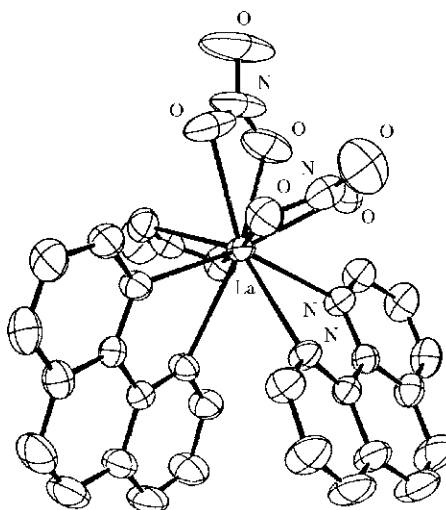
The synthesis and study of gadolinium complexes as potential magnetic resonance imaging agents is of intense interest at the moment, and is discussed in the section on MRI in Section 5.5.2.

### 4.3.9 Complexes of N-Donors

Although pyridine and similar bases are well known to form adducts with  $\beta$ -diketonate complexes, relatively few complexes of monodentate N-donors exist. Choice of solvent to restrict the oxophilic tendencies of the lanthanides is important. Thus, ammine complexes,  $[\text{Yb}(\text{NH}_3)_8][\text{Cu}(\text{S}_4)_2] \cdot \text{NH}_3$ ,  $[\text{Yb}(\text{NH}_3)_8][\text{Ag}(\text{S}_4)_2] \cdot 2\text{NH}_3$ , and  $[\text{La}(\text{NH}_3)_9][\text{Cu}(\text{S}_4)_2]$  have been synthesized by reactions in supercritical ammonia. Direct reaction of the lanthanide halides with pyridine gives pyridine complexes of the lanthanides, with the synthesis of  $[\text{YCl}_3\text{py}_4]$  and  $[\text{LnCl}_3\text{py}_4] \cdot 0.5\text{py}$  ( $\text{Ln} = \text{La}, \text{Er}$ ). These all have pentagonal bipyramidal structures, with two chlorines occupying the axial positions.  $[\text{Ml}_3\text{py}_4]$  ( $\text{M} = \text{Ce}, \text{Nd}$ ) and  $\text{EuCl}_3\text{py}_4$  have also been reported, whilst square antiprismatic  $[\text{Sm}(\text{meim})_8]\text{I}_3$  and a few other N-methylimidazole complexes such as  $[\text{YX}_2(\text{N-meim})_5]^+ \text{X}^-$  ( $\text{X} = \text{Cl}, \text{Br}$ ) have also been made.

In the case of thiocyanate complexes, a wide variety of species of known structure have been made, including  $(\text{Bu}_4\text{N})_3[\text{M}(\text{NCS})_6]$  ( $\text{M} = \text{Y}, \text{Pr} - \text{Yb}$ ; octahedral coordination);  $(\text{Et}_4\text{N})_4[\text{M}(\text{NCS})_7] \cdot \text{benzene}$  ( $\text{M} = \text{La}, \text{Pr}$ ; capped trigonal prismatic);  $(\text{Me}_4\text{N})_4[\text{M}(\text{NCS})_7] \cdot \text{benzene}$  ( $\text{M} = \text{Dy}, \text{Er}, \text{Tb}$ ; pentagonal bipyramidal); and  $(\text{Me}_4\text{N})_5[\text{M}(\text{NCS})_8] \cdot \text{benzene}$  ( $\text{M} = \text{La} - \text{Dy}$ ; intermediate between square antiprism and cubic), showing the dependence of coordination number in the solid state upon factors such as the counter-ion.

The best examples of complexes with bidentate N-donors are those with 2,2'-bipyridyl (bipy) and 1,10-phenanthroline (phen). Complexes  $\text{LnL}_2(\text{NO}_3)_3$  ( $\text{L} = \text{bipy}, \text{phen}$ ) have been studied in detail and have 10-coordinate structures with all nitrates bidentate



**Figure 4.6**

The structure of  $\text{La}(\text{phen})_2(\text{NO}_3)_3$  (reproduced by permission of the American Chemical Society from M. Frechette, I.R. Butler, R. Hynes, and C. Detellier, *Inorg. Chem.*, 1992, **31**, 1650).

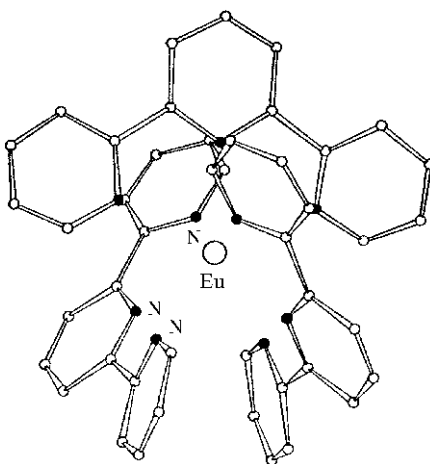
(Figure 4.6).  $\text{Ln}(\text{bipy})_3(\text{NO}_3)_3$  are in fact  $\text{Ln}(\text{bipy})_2(\text{NO}_3)_3 \cdot \text{bipy}$  (X-ray for Nd). Thiocyanates  $\text{LnL}_3(\text{NCS})_3$  ( $\text{Ln} = \text{Pr}$ ;  $\text{L} = \text{phen, bipy}$ ) have nine-coordinate monomeric structures, whilst chloride complexes with a range of structures include  $[\text{Nd}(\text{bipy})_2\text{Cl}_3(\text{OH}_2)] \cdot \text{EtOH}$  and  $[\text{Yb}(\text{bipy})_2\text{Cl}_3]$ .

Tridentate N-donor ligands are efficient in separating actinides from lanthanides selectively by solvent extraction, an area of potential great importance in treatment of used nuclear fuel rods. The tridentate ligand 2,2':6',2''-terpyridyl (terpy) forms a range of complexes. The perchlorate complexes  $[\text{Ln}(\text{terpy})_3](\text{ClO}_4)_3$  contain nine-coordinate cations with near- $D_3$  symmetry, a structure initially deduced from the fluorescence spectrum of the europium compound (Section 5.4) and subsequently confirmed by X-ray diffraction studies (Figure 4.7)

A number of chloride complexes include  $\text{Pr}(\text{terpy})\text{Cl}_3 \cdot 8\text{H}_2\text{O}$ ; X-ray diffraction established the presence of a  $[\text{Pr}(\text{terpy})\text{Cl}(\text{H}_2\text{O})_5]^{2+}$  ion. Lanthanide nitrates react with 1 mole of terpy in MeCN to give  $[\text{Ln}(\text{terpy})(\text{NO}_3)_3(\text{H}_2\text{O})_n]$  ( $\text{Ln} = \text{La}$ ,  $n = 2$ ;  $\text{Ln} = \text{Ce-Ho}$ ,  $n = 1$ ;  $\text{Ln} = \text{Er-Lu}$ ,  $n = 0$ ) with coordination numbers decreasing from 11 (La) to 9 (Er-Lu); if these are crystallized from water  $[\text{Ln}(\text{terpy})(\text{NO}_3)_2(\text{H}_2\text{O})_4]\text{NO}_3$  ( $\text{Ln} = \text{La-Gd}$ ) and  $[\text{Ln}(\text{terpy})(\text{NO}_3)_2(\text{H}_2\text{O})_3]\text{NO}_3 \cdot 2\text{H}_2\text{O}$  ( $\text{Ln} = \text{Tb-Lu}$ ) are formed; these have both bidentate and ionic nitrate and nine- and eight-coordinate lanthanides, respectively. Thiocyanate complexes  $\text{Ln}(\text{terpy})_2(\text{NCS})_3$  ( $\text{Ln} = \text{Pr, Nd}$ ) are also nine coordinate.

#### 4.3.10 Complexes of Porphyrins and Related Systems

One convenient synthesis of these compounds involves heating  $\text{La}(\text{acac})_3$  with  $\text{H}_2\text{TPP}$  ( $\text{H}_2\text{TPP}$  = tetraphenylporphyrin) and other porphyrins in high-boiling solvents such as 1,3,5-trichlorobenzene (TCB). Products depend upon conditions and include  $[\text{Ln}(\text{acac})(\text{tpp})]$  and the double-decker sandwich  $[\text{Ln}_2(\text{tpp})_3]$ . Less forcing routes can be used, for example the reaction of  $[\text{Y}\{\text{CH}(\text{SiMe}_3)_2\}_3]$  and yttrium alkoxides with  $\text{H}_2\text{OEP}$

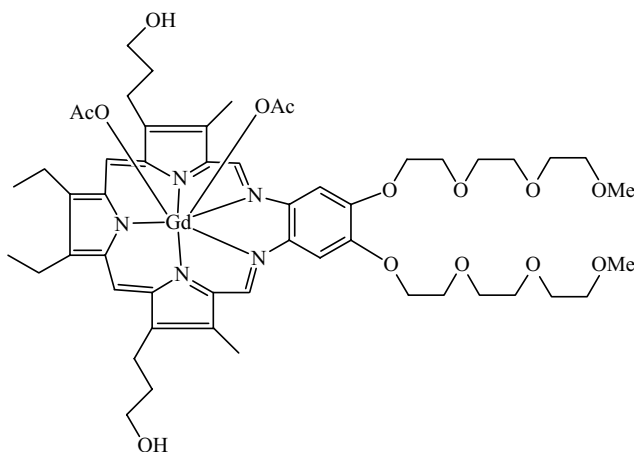
**Figure 4.7**

The structure of  $\text{Eu}(\text{terpy})_3^{3+}$  (reproduced by permission of the Royal Society of Chemistry from G.H. Frost, F.A. Hart, C. Heath, and M.B. Hursthouse, *Chem. Commun.*, 1969, 1421).

(octaethylporphyrin) to form compounds like  $[\text{Y}\{\text{CH}(\text{SiMe}_3)_2\}(\text{Oep})]$ . Bis(porphyrin) complexes and mixed (porphyrin)phthalocyanine complexes are probably complexes of the trivalent lanthanide where one ligand is a dianion and another a one-electron-oxidized  $\pi$ -radical, as in  $[\text{Ln}^{\text{III}}(\text{pc})(\text{tpp})]$  ( $\text{Ln} = \text{La}, \text{Pr}, \text{Nd}, \text{Eu}, \text{Gd}, \text{Er}, \text{Lu}, \text{Y}$ ).

Complexes, particularly of gadolinium, with a  $\text{N}_4$ -donor macrocycle backbone that also supports carboxylate groups have assumed importance in the context of MRI contrast agents (Sections 5.5.2 and 5.5.3).

Gadolinium texaphyrin (Gd-tex; Figure 4.8) is reported to be an effective radiation sensitizer for tumour cells, whilst the corresponding lutetium compound, which absorbs light in the far-red end of the visible spectrum, is in Phase II trials for photodynamic therapy for brain tumours and breast cancer.

**Figure 4.8**

Gd-tex.

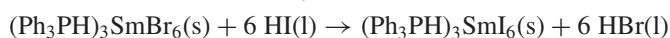
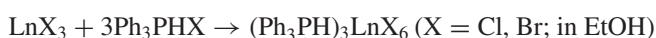
### 4.3.11 Halide Complexes

Complexes with all the halide ions have been made, though the fluorides and chlorides are the most studied. Fluorides  $\text{ALnF}_4$ ,  $\text{A}_2\text{LnF}_5$  and  $\text{A}_3\text{LnF}_6$  exist ( $\text{A} = \text{alkali metal}$ ); most have structures with 8- or 9-coordinate metals, though a few  $\text{A}_3\text{LnF}_6$  have the six-coordinate cryolite structure.

$\text{Cs}_2\text{LiLnCl}_6$  are an important type of complex.



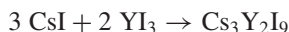
Made by fusion, they possess the six-coordinate elpasolite structure in which the perfectly octahedral  $[\text{LnCl}_6]^{3-}$  ions occupy sites with cubic symmetry. These have been much studied for their optical and magnetic properties on account of this, the  $\text{Ln}^{3+}$  ions on their highly symmetrical sites having especially weak f–f transitions in their electronic spectra. Some other  $\text{A}_2\text{BMX}_6$  systems also adopt the elpasolite structure. Other halide complexes like  $(\text{Ph}_3\text{PH})_3(\text{LnX}_6)$  and  $(\text{pyH})_3(\text{LnX}_6)$  ( $\text{X} = \text{Cl, Br, I}$ ) have been made by solution methods:



The iodides are hygroscopic and rather unstable. Other stoichiometries are possible:



including species with more than one lanthanide ion:



Six coordination is the norm for chlorides, bromides, and iodides, but it is not invariable. Formulae are not necessarily a guide to the species present; thus, octahedral  $[\text{YbCl}_6]^{3-}$  ions are present in  $\text{M}_4\text{YbCl}_7$  ( $\text{M} = \text{Cs, MeNH}_3$ ) but  $\text{Ba}_2\text{EuCl}_7$  contains capped trigonal prismatic  $[\text{EuCl}_7]^{4-}$  ions. Compounds like  $\text{Cs}_2\text{Y}_2\text{I}_9$  attain six coordination through face-sharing of octahedra,  $\text{Cs}_2\text{DyCl}_5$  has corner-sharing of octahedra, and  $\text{M}_2\text{PrBr}_5$  ( $\text{M} = \text{K, NH}_4$ ) obtain seven coordination though edge-sharing. Structure type can depend on temperature; thus,  $\text{NaLnCl}_4$  ( $\text{Ln} = \text{Eu–Yb, Y}$ ) have the six-coordinate  $\alpha$ - $\text{NiWO}_4$  structure at low temperature and the seven-coordinate  $\text{NaGdCl}_4$  structure at high temperatures. To summarize, although rewarding study over many years for the variety of structures adopted and the opportunities to study optical and magnetic properties, the area of complex halides is complicated and each case has to be judged on its own merits.

### 4.3.12 Complexes of S-Donors

As a ‘soft’ donor, sulfur is not expected to complex well with lanthanides; nevertheless a number of complexes have been isolated through working in nonpolar solvents. The simplest of these complexes are the dithiocarbamates  $\text{Ln}(\text{S}_2\text{CNR}_2)_3$  and related dithiophosphates  $\text{Ln}(\text{S}_2\text{PR}_2)_3$ ; of the latter,  $\text{Ln}[\text{S}_2\text{P}(\text{cyclohexyl})_2]_3$  ( $\text{Ln} = \text{Pr, Sm}$ ) have trigonal prismatic geometries. The dithiocarbamates form more stable 8-coordinate adducts  $\text{Ln}(\text{S}_2\text{CNR}_2)_3 \cdot \text{bipy}$  ( $\text{R} = \text{Me, Et}$ ) and anionic species  $[\text{Ln}(\text{S}_2\text{CNR}_2)_4]^-$ . A range of geometries are known in the solid state: distorted dodecahedral  $\text{Et}_4\text{N}[\text{Eu}(\text{S}_2\text{CNEt}_2)_4]$ ,  $\text{Na}[\text{Eu}(\text{S}_2\text{CNEt}_2)_4]$ , near-perfect dodecahedral  $(\text{Ph}_4\text{As})[\text{Ln}(\text{S}_2\text{PEt}_2)_4]$ , and square antiprismatic  $\text{Ph}_4\text{P} [\text{Pr}(\text{S}_2\text{PMe}_2)_4]$ .

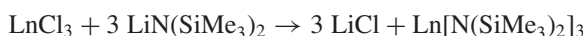
A number of lanthanide thiolates have been synthesized in recent years and are discussed in Section 4.4.3.

## 4.4 Alkoxides, Alkylamides and Related Substances

Some of these compounds have been known for over 30 years, but interest in the former in particular has been stimulated recently by their potential use as precursors for deposition of metal oxides using the sol-gel or MOCVD process. These compounds are particularly interesting insofar as many of them involve very bulky ligands and therefore have low coordination numbers (see Section 4.5).

### 4.4.1 Alkylamides

The volatile air-sensitive silylamides  $\text{Ln}[\text{N}(\text{SiMe}_3)_2]_3$  are the best-characterized alkylamides. They are made by salt-elimination reactions in a solvent like THF:



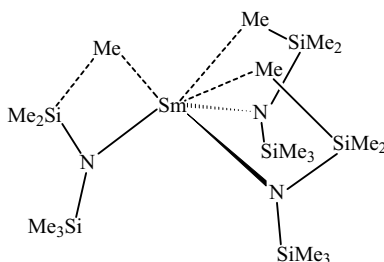
They are volatile *in vacuo* at 100 °C and dissolve in hydrocarbons; the first three-coordinate lanthanide compounds to be characterized, they have congested three-coordinate geometries (Figure 4.9) due to the bulky  $\text{SiMe}_3$  groups. They are pyramidal in the solid state with N–Ln–N angles around 114° rather than the 120° expected for a planar structure but they are evidently planar in solution as they have no dipole moment. Theoretical calculations (D.L. Clark *et al.*, 2002; L. Penin *et al.*, 2002) indicate that it is  $\beta$ -Si–C agostic interactions with the lanthanide that are responsible for this small pyramidal distortion.

$\text{Ln}[\text{N}(\text{SiMe}_3)_2]_3$  form stable four-coordinate  $\text{Ph}_3\text{PO}$  and  $\text{Ph}_2\text{CO}$  adducts; when excess of phosphine oxide is used, five-coordinate peroxide-bridged dimers are obtained.  $\text{Eu}[\text{N}(\text{SiMe}_3)_2]_3$  forms both 1:1 and 1:2 adducts with  $\text{Me}_3\text{PO}$ . They are capable of binding two very small MeCN groups, the latter reversibly, but no thf adducts have been isolated.

When a deficit of the lithium alkylamide is used, dimeric chloride-bridged silylamides are obtained which are useful synthetic intermediates (Figure 4.10).

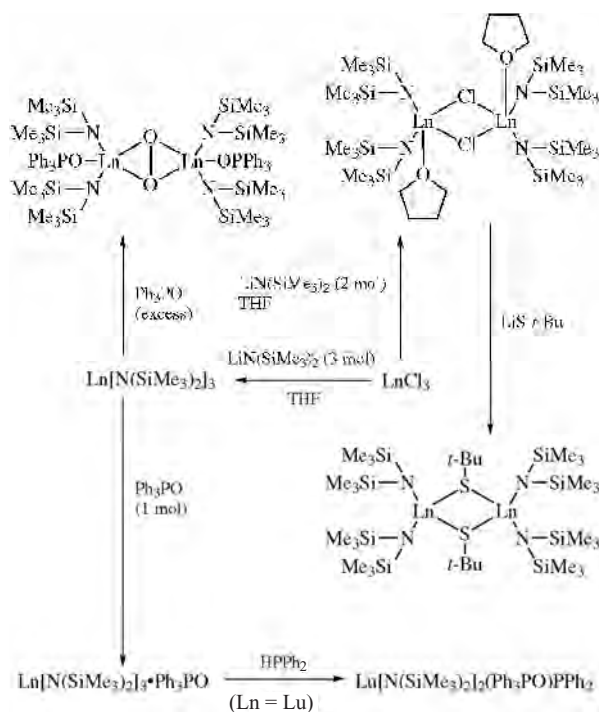
Using less bulky alkyl substituents, compounds  $[\text{Ln}(\text{N}(\text{SiHMe}_2)_2)_3(\text{thf})_2]$  have been made for La–Lu, Y. These have trigonal bipyramidal structures with axial thf molecules {the scandium analogue is pseudo-tetrahedral  $\text{Sc}[\text{N}(\text{SiHMe}_2)_2]_3(\text{thf})$ }. Other alkylamides  $\text{Ln}(\text{NPr}^i)_3$  (Ln = La, Nd, Yb, Y, Lu) are obtained with the less hindered isopropylamide ligand; these compounds form isolable thf adducts. Simple dimethylamides cannot be obtained, as reaction of  $\text{LnCl}_3$  with  $\text{LiNMe}_2$  gives  $\text{Ln}(\text{NMe}_2)_3$  as LiCl adducts.

Use of a highly fluorinated amide has permitted the synthesis of  $[\text{Sm}[\text{N}(\text{SiMe}_3)(\text{C}_6\text{F}_5)]_3]$  in which there are many Sm...F and agostic interactions (Figure 4.11), so that the true coordination number of the metal is really greater than three.

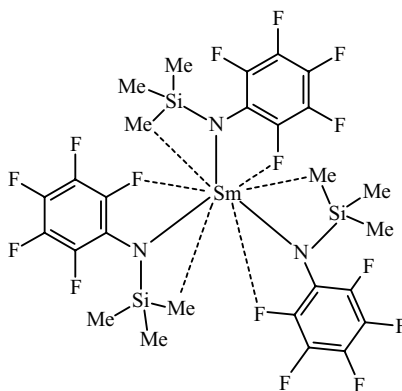


**Figure 4.9**  
The structure of  $\text{Ln}[\text{N}(\text{SiMe}_3)_2]_3$ .





**Figure 4.10**  
Lanthanide bis(trimethylsilyl)amido complexes.

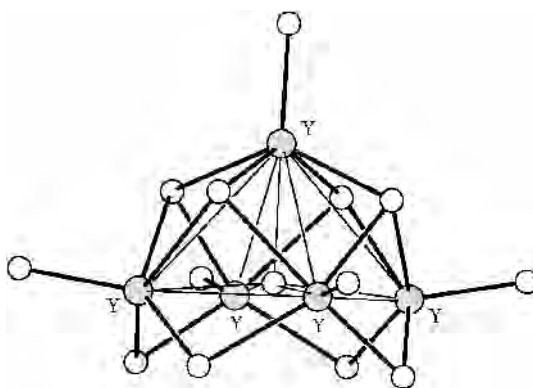


**Figure 4.11**  
The structure of  $[\text{Ln}[\text{N}(\text{SiMe}_3)(\text{C}_6\text{F}_5)]_3]$ .

The neodymium compound  $[(\eta^6\text{-C}_6\text{H}_5\text{Me})\text{Nd}\{\text{N}(\text{C}_6\text{F}_5)_2\}_3]$  has a  $\eta^6$ -bonded toluene molecule with a distorted piano-stool geometry.

#### 4.4.2 Alkoxides

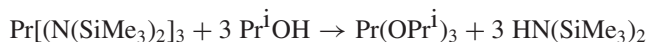
The simplest lanthanide alkoxide compounds about which much is known are the isopropoxides. There is some evidence that under mild conditions a simple  $\text{Ln}(\text{OPr}^i)_3$  can be

**Figure 4.12**

The structure of  $\text{Y}_5\text{O}(\text{OPr}^i)_{13}$  (reproduced by permission of the American Chemical Society from O. Poncelet, O.W.J. Sartain, L.G. Hubert-Pfalzgraf, K. Folting, and K.G. Caulton, *Inorg. Chem.*, 1989, **28**, 264).

formed, but the product generally obtained from synthesis [which may be described by the synthesizers as ' $\text{Ln}(\text{OPr}^i)_3$ '] is an oxo-centred cluster  $\text{Ln}_5\text{O}(\text{OPr}^i)_{13}$  (Figure 4.12) (X-ray for Y, Er, Yb, etc.) with a square-pyramidal core.

Syntheses include:



The reaction conditions for syntheses seem important, as a chlorine-containing cluster  $\text{Nd}_6(\text{OPr}^i)_{17}\text{Cl}$  has also been reported, from the reaction of  $\text{NdCl}_3$  with  $\text{NaOPr}^i$ . Alkoxides of known structure include  $\text{Ln}(\text{OCH}_2\text{Bu}^t)_3$ , which is a tetramer ( $\text{Ln} = \text{La}, \text{Nd}$ ), based on a square of lanthanide atoms with bridging alkoxides and no direct metal-metal bonds [ $\text{Ln}_4(\mu_2\text{-OR})_8(\text{OR})_4$ ] ( $\text{R} = \text{CH}_2\text{Bu}^t$ ).  $\text{La}(\text{OBu}^t)_3$  was isolated as a trimer containing a triangle of lanthanum atoms (and two coordinated alcohol molecules) [ $\text{La}_3(\mu_3\text{-OBu}^t)_3(\mu_2\text{-OBu}^t)_3(\text{OBu}^t)_4(\text{Bu}^t\text{OH})_2$ ];  $\text{Nd}(\text{OCHPr}^i)_3$  has been isolated as a dimeric solvate [ $\text{Nd}_2(\mu_2\text{-OR})_2(\text{OR})_4\text{L}_2$ ] ( $\text{L} = \text{py}, \text{thf}$ ).  $\text{Ce}(\text{OBu}^t)_3$  is believed to be a monomer. It undergoes thermolysis in high yield.

Dimeric structures are also exhibited by [ $\text{Ln}(\text{OQPh})_3$ ] $_2$  ( $\text{Ln} = \text{La}, \text{Ce}, \text{Y}$ ;  $\text{Q} = \text{C}, \text{Si}$ ), though the bridges are cleaved by Lewis bases, forming adducts such as  $\text{Ln}(\text{OSiPh})_3(\text{thf})_3$  (*fac*-octahedral;  $\text{Ln} = \text{Y}, \text{La}, \text{Ce}$ ) and  $\text{Y}(\text{OSiPh})_3(\text{OPBu}_3)_2$  (*tbp*).

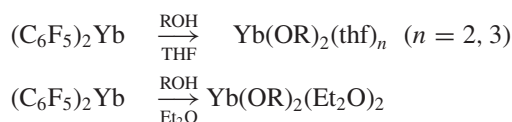
A range of aryloxides has been made. The diphenylphenoxides  $\text{Ln}(\text{OR})_3$  ( $\text{R} = 2,6\text{-Ph}_2\text{C}_6\text{H}_3\text{O}$ ) have three-coordinate pyramidal structures with some additional Ln–ring interactions. When the bulk of the aryloxide is increased by putting two tert-butyl groups into the 2,6-positions of the benzene ring, three-coordinate aryloxides  $\text{Ln}(\text{O-2,6-Bu}_2\text{-4-RC}_6\text{H}_2)_3$  can be isolated ( $\text{R} = \text{H}$ ,  $\text{Ln} = \text{Y}, \text{La}, \text{Sm}$ ;  $\text{R} = \text{Me}$ ,  $\text{Ln} = \text{Y}, \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Dy-Er}, \text{Yb}$ ). Trigonal planar geometry is found in  $\text{Y}(\text{O-2,6-Bu}_2\text{-4-C}_6\text{H}_3)_3$  but a pyramidal structure is adopted in  $\text{Ce}(\text{O-2,6-Bu}_2\text{-4-MeC}_6\text{H}_2)_3$ . Synthesis of  $\text{Nd}(\text{Odpp})_3$  in THF gives [ $\text{Nd}(\text{Odpp})_3(\text{thf})_2$ ], which crystallizes from toluene as [ $\text{Nd}(\text{Odpp})_3(\text{thf})$ ] and sublimates as [ $\text{Nd}(\text{Odpp})_3$ ]. The structure of [ $\text{Nd}(\text{Odpp})_3(\text{thf})_2$ ].2THF shows it to be a five-coordinate bis(thf) complex in which the five ligands bind only by oxygen. Removal of the thf ligands affords compounds

where benzene rings additionally bond to the lanthanide. The departure of one or two electron-pair donors from the coordination sphere means that the  $\text{Ln}^{3+}$  ion accepts electron density from ligand  $\pi$  systems and in a sense 'maintains its coordination number'. (see G.B. Deacon *et al.*, *J. Chem. Soc., Dalton Trans.*, 2000, 961 for a fuller account of these unusual compounds.)

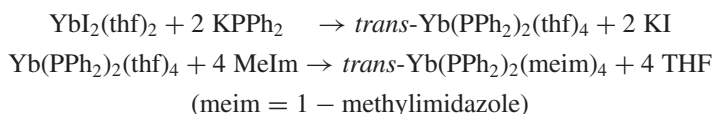
There is a more limited chemistry of alkoxides and aryloxides in the +2 and +4 states. The  $\text{Ce}^{\text{IV}}$  compounds, the only ones known in this oxidation state, are discussed in Section 4.6.2.

Much of the chemistry in the +2 state has been with aryloxides; thus 2,6-diphenylphenol (dppOH) reacts with Eu or Yb on heating in the presence of mercury, forming  $[\text{Ln}(\text{Odpp})_2]$ . These have the structures  $[\text{Eu}_2(\text{Odpp})(\mu\text{-Odpp})_3]$  and  $[\text{Yb}_2(\text{Odpp})(\mu\text{-Odpp})_3]$ .

Another route involves alcoholysis of an aryl ( $\text{R} = 2,6\text{-Bu}_2'\text{C}_6\text{H}_3\text{O}$ ):



In recent years, phosphide complexes have proved accessible:



Similar compounds have been synthesized, including *trans*- $\text{Sm}(\text{Qmes}_2)_2(\text{thf})_4$  ( $\text{Q} = \text{P, As}$ ; mes = mesityl);  $[\text{Nd}\{\text{P}(\text{SiMe}_3)_2\}_3(\text{thf})_2]$  has a trigonal bipyramidal structure.

### 4.4.3 Thiolates

Lanthanide thiolates are rare, but monomeric species have been obtained using bulky ligands, such as the three-coordinate  $\text{Sm}(\text{S-2,4,6-Bu}_3'\text{C}_6\text{H}_2)_3$  and the monomeric, *mer*- $[\text{Yb}(\text{SPh})_3\text{py}_3]$ .  $\text{Ln}(\text{SPh})_3$  reacts with S, forming octanuclear clusters  $[\text{Ln}_8\text{S}_6(\text{SPh})_{12}(\text{thf})_8]$  ( $\text{Ln} = \text{Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er}$ ); analogous pyridine clusters  $[\text{Ln}_8\text{S}_6(\text{SPh})_{12}(\text{py})_8]$  ( $\text{Ln} = \text{Nd, Sm, Er}$ ) have also been isolated.  $\text{Ph}_2\text{Se}_2$  reacts with lanthanide amalgams and pyridine, forming  $\text{Ln}(\text{SePh})_3(\text{py})_3$  ( $\text{Ln} = \text{Ho, Tm, Yb}$ ) which are dimeric with 7-coordinate lanthanides.  $[\text{Ln}(\text{SePh})_3(\text{thf})_3]$  ( $\text{Ln} = \text{Tm, Ho, Er}$ ) have monomeric *fac*-octahedral structures;  $[\text{Ln}_8\text{E}_6(\text{EPh})_{12}\text{L}_8]$  clusters ( $\text{E} = \text{S, Se}$ ;  $\text{Ln} = \text{lanthanide}$ ;  $\text{L} = \text{Lewis base}$ ) can be prepared by reduction of Se–C bonds by low-valent Ln or by reaction of  $\text{Ln}(\text{SePh})_3$ . Structures reported include  $[\text{Sm}_8\text{E}_6(\text{SPh})_{12}(\text{thf})_8]$  ( $\text{E} = \text{S, Se}$ ) and  $[\text{Sm}_8\text{Se}_6(\text{SePh})_{12}(\text{py})_8]$ ; they have cubes of lanthanide ions with  $\text{E}^{2-}$  ions capping the faces and EPh bridging the edges of the cube. Reaction of  $\text{Nd}(\text{SePh})_3$  with Se to form  $[\text{Nd}_8\text{Se}_6(\text{SePh})_{12}(\text{py})_8]$  shows that this series is not restricted to redox-active lanthanides.

## 4.5 Coordination Numbers in Lanthanide Complexes

### 4.5.1 General Principles

Ionic radii of  $\text{La}^{3+}$  and  $\text{Lu}^{3+}$  ions in octahedral coordination are 1.032 Å, and 0.861 Å, respectively. The corresponding value for the largest  $\text{M}^{3+}$  ion of a transition metal is 0.670 Å

for  $\text{Ti}^{3+}$ . Purely on steric grounds, therefore, it would be expected that lanthanide ions could accommodate more than six ligands in their coordination sphere. Coupled with this is the fact that the f-orbitals are ‘inner’ orbitals, shielded from the effects of the surrounding anions and therefore not able to participate in directional bonding; there are none of the ligand-field effects found in transition metal chemistry with the concomitant preference for octahedral coordination. In summary, the coordination number (CN) adopted by a particular complex is determined by how many ligands can be packed round the central metal ion; coordination numbers between 2 and 12 are known in lanthanide complexes. Geometries are those corresponding to the simple polyhedra that would be predicted from electron-pair repulsion models; tetrahedral (CN 4), trigonal bipyramidal (CN 5), octahedral (CN 6); though with coordination numbers 2 and 3 deviations from simple linear and trigonal planar geometries in the solid state often occur (and are probably due to agostic interactions).

Some 20 years ago, analysis of the coordination numbers for large numbers of coordination compounds of yttrium and the lanthanides indicated that coordination numbers of 8 and 9 are almost equally common, accounting for around 60% of the known structures, and it is unlikely that this distribution has changed significantly. As already pointed out, it is steric factors that determine the coordination number (and geometry) adopted by a lanthanide ion (see e.g. X.-Z. Feng, A.-L. Guo, Y.-T. Xu, X.-F. Li and P.-N. Sun, *Polyhedron*, 1987, **6**, 1041; J. Marçalo and A. Pires de Matos, *Polyhedron*, 1989, **8**, 2431). Saturation in the coordination sphere of the metal can come about in one of two ways.

### First-Order Effects

When small ligands like water or chloride bind to a metal, the coordination number is determined by how many ligands can pack round the central metal ion, a number relating to repulsion between the donor atoms directly in contact with the metal, a so-called ‘first-order’ effect.

### Second-Order Effects

Certain ‘bulky’ ligands have a small donor atom (N, O, C) attached to bulky substituents, examples being certain alkoxides and aryloxides (and related systems), bis(trimethylsilyl)amido [ $-\text{N}(\text{SiMe}_3)_2$ ], and the isolobal alkyl [ $-\text{CH}(\text{SiMe}_3)_2$ ]; and mesityl. These ligands have high second-order steric effects generating crowding round the lanthanide; even though the metal ion is bound to few donor atoms, the bulk of the rest of the ligand shields the metal from other would-be ligands.

Species like  $\text{LnCl}_6^{3-}$  and  $[\text{Ln}(\text{H}_2\text{O})_9]^{3+}$  are examples where first-order effects determine the coordination number, whilst  $\text{Ln}[\text{CH}(\text{SiMe}_3)_2]_3$  and  $[\text{Ln}\{\text{N}(\text{SiMe}_3)_2\}_3(\text{Ph}_3\text{PO})]$  are cases where the bulky substituents on the amide and alkyl ligands with high second-order steric effects generate crowding round the lanthanide.

## 4.5.2 Examples of the Coordination Numbers

### Coordination Number 2

Coordination number 2 is represented by the sublimeable two coordinate bent alkyl  $[\text{Yb}\{\text{C}(\text{SiMe}_3)_3\}_2]$  (C–Yb–C 137°) and the europium analogue. Although there are only two Yb–C  $\sigma$  bonds, the bending is caused by a number of agostic Yb...H–C interactions

(a similar situation applying to some zerovalent Pd and Pt phosphine complexes  $M(PR_3)_2$ , where R is a bulky group like  $Bu^t$  or cyclohexyl).

### Coordination Number 3

This is best illustrated by some alkyl and alkylamide  $LnX_3$  systems {X = a bulky group such as  $-N(SiMe_3)_2$ ,  $-CH(SiMe_3)_2$ , e.g.  $Ln[CH(SiMe_3)_2]_3$  ( $Ln = Y, La, Pr, Nd, Sm, Lu$ );  $Ln[N(SiMe_3)_2]_3$ , ( $Ln = Y$ , all lanthanides)}. Many transition metals form analogous, planar, three-coordinate alkylamides; the majority of these lanthanide compounds have pyramidal structures in the solid state [but are generally planar in the gas phase and in solution (they have zero dipole moment)]. These distortions appear to involve agostic interactions. Certain alkoxides and aryloxides  $Ln(OR)_3$  are formed using bulky ligands (e.g.  $Ln = Ce$ ;  $R = 2,6-Bu_2C_6H_3O$ ).

### Coordination Number 4

A few four-coordinate compounds are known, such as  $Ln[(N(SiMe_3)_2)_3.(Ph_3PO)]$ ,  $[Li(thf)_4][Ln(NPh_2)_4]$  ( $Ln = Er, Yb$ ),  $[Li(thf)_4][Lu(2,6-dimethylphenyl)_4]$ , and  $Li(THF)_4[Ln(CH_2SiMe_3)_4]$  ( $Ln = Y, Er, Tb, Yb$ ); there is a tetrahedral geometry as expected. Again, the ligands have high second-order steric effects generating crowding round the lanthanide even though there are only four atoms bound to the lanthanide.

### Coordination Number 5

As yet this is a rare coordination number. The three-coordinate silylamides can add two slender ligands to form five-coordinate examples  $Ln[N(SiMe_3)_2]_3(NCMe)_2$ , whilst there are a few alkyls e.g.  $Yb(CH_2Bu^t)_3(thf)_2$ .  $[Nd\{P(SiMe_3)_2\}_3(thf)_2]$  has also been described. These have trigonal bipyramidal structures, as expected.

### Coordination Number 6

Salts  $Cs_2LiLnCl_6$  ( $Ln = La-Lu$ ) have the elpasolite structure with  $[LnCl_6]^{3-}$  anions on cubic sites; this geometry could be due to first-order crowding among the six chlorides, but some other salts are known where  $LnCl_7$  units occur. Other examples include the reactive alkyls  $[Li(L-L)_3][Ln(CH_3)_6]$  ( $L-L = MeOCH_2CH_2OMe$  or  $Me_2NCH_2CH_2NMe_2$ ;  $Ln = La-Sm, Gd-Lu, Y$ ) and diketonates of bulky ligands such as  $[Ln(Bu^tCOCHCOBu^t)_3]$  ( $Ln = Tb-Lu$ ). Some compounds have geometry distorted to trigonal prismatic because of steric interactions between ligands, such as  $[Ln\{S_2P(cyclohexyl)_2\}_3]$ . Some thiocyanate complexes  $(Bu_4N)_3[M(NCS)_6]$  ( $M = Y, Pr-Yb$ ) have octahedral coordination (Section 4.3.9) but others like  $(Et_4N)_4[M(NCS)_7].benzene$  ( $M = La, Pr$ ) and  $(Me_4N)_5[M(NCS)_8].benzene$  ( $M = La-Dy$ ) are 7- and 8-coordinate, respectively, a reminder that the coordination number adopted depends upon a subtle balance between factors, including the counter-ion and solvent.

### Coordination Number 7

The most common geometries encountered are capped octahedral and capped trigonal prismatic. Many of the known seven-coordinate compounds involve  $\beta$ -diketonate ligands, particularly adducts of the type  $Ln(diketonate)_3.L$  ( $L =$  Lewis base e.g.  $H_2O, py$ ). Several

thf complexes (Section 4.3.3) of the type  $\text{Ln}(\text{thf})_4\text{X}_3$  ( $\text{X} = \text{Cl}, \text{NCS}$ ) adopt pentagonal bipyramidal geometries), as does the ytterbium(II) aryl  $[\text{Yb}(\text{C}_6\text{F}_5)_2(\text{thf})_5]$ .  $\text{Ba}_2\text{EuCl}_7$  has capped trigonal prismatic  $[\text{EuCl}_7]^{4-}$  ions. The energy difference between these two geometries is small, witness  $(\text{Et}_4\text{N})_4 [\text{M}(\text{NCS})_7]\cdot\text{benzene}$  ( $\text{M} = \text{La}, \text{Pr}$ : capped trigonal prismatic) and  $(\text{Me}_4\text{N})_4 [\text{M}(\text{NCS})_7]\cdot\text{benzene}$  ( $\text{M} = \text{Dy}, \text{Er}, \text{Tb}$ : pentagonal bipyramidal).

### Coordination Number 8

Most eight-coordinate lanthanide complexes have dodecahedral or square antiprismatic geometries. The energy difference between these is likely to be small, witness the distorted dodecahedral  $\text{Et}_4\text{N} [\text{Eu}(\text{S}_2\text{CNEt}_2)_4]$ , near-perfect dodecahedral  $(\text{Ph}_4\text{As})[\text{Ln}(\text{S}_2\text{PEt}_2)_4]$ , and square antiprismatic  $\text{Ph}_4\text{P} [\text{Pr}(\text{S}_2\text{PMe}_2)_4]$ . Similarly, among eight-coordinate thiocyanate complexes,  $(\text{Me}_4\text{N})_5 [\text{M}(\text{NCS})_8]\cdot\text{benzene}$  ( $\text{M} = \text{La-Dy}$ ) are intermediate between square antiprism and cubic;  $(\text{Et}_4\text{N}) [\text{M}(\text{NCS})_4(\text{H}_2\text{O})_4]$  ( $\text{M} = \text{Nd}, \text{Eu}$ ) and  $(\text{Me}_4\text{N})_3 [\text{M}(\text{NCS})_6(\text{H}_2\text{O})(\text{MeOH})]$  ( $\text{M} = \text{La-Dy}, \text{Er}$ ) are square antiprismatic;  $(\text{Et}_4\text{N})_4 [\text{M}(\text{NCS})_7(\text{H}_2\text{O})]$  ( $\text{M} = \text{La-Nd}, \text{Dy}, \text{Er}$ ) are cubic; and  $(\text{Me}_4\text{N})_5 [\text{M}(\text{NCS})_8]\cdot\text{benzene}$  ( $\text{M} = \text{La-Dy}$ ) are intermediate between square antiprismatic and cubic.

### Coordination Number 9

Tricapped trigonal prismatic is the most familiar example of nine-coordinate geometry, adopted for the  $[\text{Ln}(\text{H}_2\text{O})_9]^{3+}$  ions of all lanthanides in a number of crystalline salts. It is also found in a number of chlorides  $\text{LnCl}_3$  ( $\text{Ln} = \text{La-Gd}$ ) and bromides  $\text{LnBr}_3$  ( $\text{Ln} = \text{La-Pr}$ ). This geometry is also sometimes adopted where polydentate ligands are involved, such as the  $[\text{Ln}(\text{terpy})_3]^{3+}$  ion ( $\text{terpy} = 2,2':6',2''\text{-terpyridyl}$ ; see Figure 4.7).

### Coordination Numbers 10–12

Sheer congestion of donor atoms around the metal ion and concomitant inter-donor atom repulsions makes these high coordination numbers difficult to attain. They are often associated with multidentate ligands with a small ‘bite angle’ such as nitrate that take up little space in the coordination sphere, either alone, as in  $(\text{Ph}_4\text{As})_2[\text{Eu}(\text{NO}_3)_5]$  or in combination with other ligands, as in  $\text{Ln}(\text{bipy})_2(\text{NO}_3)_3$ ,  $\text{Ln}(\text{terpy})(\text{NO}_3)_3(\text{H}_2\text{O})$  ( $\text{Ln} = \text{Ce-Ho}$ ), and crown ether complexes (Section 4.3.7) such as  $\text{Ln}(\text{12-crown-4})(\text{NO}_3)_3$  ( $\text{Ln} = \text{Nd-Lu}$ ). Other crown ether complexes can have 11 and 12 coordination, e.g.  $\text{Eu}(\text{15-crown-5})(\text{NO}_3)_3$  ( $\text{Ln} = \text{Nd-Lu}$ ) and  $\text{Ln}(\text{18-crown-6})(\text{NO}_3)_3$  ( $\text{Ln} = \text{La}, \text{Nd}$ ).

Polyhedra in these high coordination numbers are often necessarily irregular, but when all the ligands are identical, near-icosahedral geometries occur for the 12-coordinate  $[\text{Pr}(\text{1,8-naphthyridine})_6]^{3+}$  and  $[\text{La}(\text{NO}_3)_6]^{3-}$  ions in crystalline salts. It should also be remembered that the geometries discussed here are found in the solid state, but on dissolution in a solvent, where the influence of counter-ions is lessened, matters may be different (see the aqua ions, Sections 4.3.1 and 4.3.2). In principle, isomers are often possible, but because of the lability of lanthanide complexes they are very rarely observed.

## 4.5.3 The Lanthanide Contraction and Coordination Numbers

Certain *generalizations* can be made. As noted elsewhere (Section 2.4) the contraction of the  $(5s^2 5p^6)$  configuration with increasing nuclear charge, due to penetration inside the

f-orbitals, means that the  $\text{Ln}^{3+}$  (and  $\text{Ln}^{2+}$ ) ions become smaller as the atomic number increases. Because of the decrease in ionic radius as the atomic number of the lanthanide increases, it would be expected that fewer anions could be packed round the central metal ion as the ionic radius decreases; in other words, that the coordination number will decrease with increasing Z. It may similarly be predicted that the coordination number would decrease with increasing size of the anion. This behaviour is clearly observed in the halides and oxides (Chapter 3). To reiterate, in the fluorides  $\text{LnF}_3$ , the coordination number decreases from 11 in  $\text{LaF}_3$  through 9 in  $\text{SmF}_3$ ; similarly in the trichlorides, lanthanum is 9 coordinate in  $\text{LaCl}_3$  but lutetium is 6 coordinate in  $\text{LuCl}_3$ . The coordination number of lutetium decreases from 9 in  $\text{LuF}_3$  to 6 in  $\text{LuI}_3$ . Similar changes in coordination number are found in many complexes, the best known example being the hydrated  $\text{Ln}^{3+}(\text{aq})$  ion. Nine-coordinate  $[\text{Ln}(\text{OH}_2)_9]^{3+}$  ions are found in solution for the earlier metals ( $\text{Ln} = \text{La}-\text{Sm}/\text{Eu}$ ) and eight-coordinate  $[\text{Ln}(\text{OH}_2)_8]^{3+}$  ions for later metals ( $\text{Dy}-\text{Lu}$ , Y) with a mixture of species for the intermediate metals.

This decrease in coordination number is not an invariable rule, as examples are known where the coordination number remains constant across the series, as in  $\text{Ln}(\text{bipy})_2(\text{NO}_3)_3$  and  $\text{Ln}(\text{phen})_2(\text{NO}_3)_3$  ( $\text{Ln} = \text{La}-\text{Lu}$ ) where all are 10 coordinate in the solid state, or  $\text{Ln}(\text{hmpa})_3\text{Cl}_3$ , all of which appear to be 6 coordinate. When bidentate ligands are involved, loss of one of them may produce a too dramatic change in CN. The influence of a counterion, which will affect the lattice energy and hence the solubility, determining which complex species crystallizes first, can also be important. The best example of this lies in the crystalline hydrated salts of several oxoacids  $[\text{Ln}(\text{OH}_2)_9]\text{X}_3$  ( $\text{Ln} = \text{La}-\text{Lu}$ , Y; X e.g.  $\text{BrO}_3$ ,  $\text{CF}_3\text{SO}_3$ ,  $\text{C}_2\text{H}_5\text{SO}_4$ ) all of which contain the  $[\text{Ln}(\text{OH}_2)_9]^{3+}$  ion, whereas the coordination number of the  $\text{Ln}^{3+}(\text{aq})$  ion varies in solution, as noted above. In contrast, the perchlorates  $\text{Ln}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$  contain octahedral  $[\text{Ln}(\text{OH}_2)_6]^{3+}$  ions. Similarly, in the edta complexes  $\text{M}[\text{Ln}(\text{edta})(\text{H}_2\text{O})_x]$ , nine-coordinate  $[\text{Ho}(\text{edta})(\text{H}_2\text{O})_3]^-$  ions are found in the crystal when  $\text{M} = \text{K}$  whilst eight-coordinate  $[\text{Ho}(\text{edta})(\text{H}_2\text{O})_2]^-$  ions are found when  $\text{M} = \text{Cs}$ .

#### 4.5.4 Formulae and Coordination Numbers

Many transition metals adopt characteristic coordination numbers in their compounds, and consequently it is often possible to deduce whether (and how) a potential ligand will coordinate or not. The lanthanides do not have characteristic coordination numbers, so such assumptions are not possible; ultimately, X-ray diffraction studies are the only sure guide. The presence of coordinated solvent molecules in crystals obtained from polar solvents is generally best deduced thus, hence the assignment of an 8-coordinate structure to  $[\text{LaCl}_3(\text{phen})_2(\text{H}_2\text{O})]\cdot\text{MeOH}$ . Likewise  $\text{La}(\text{phen})_3\text{Cl}_3 \cdot 9\text{H}_2\text{O}$  has been shown to be  $[\text{La}(\text{phen})_2(\text{OH}_2)_3]\text{Cl}_3 \cdot 4\text{H}_2\text{O} \cdot \text{phen}$ .  $[\text{Sm}(\text{NO}_3)_3(\text{Ph}_3\text{PO})_3] \cdot 2$  acetone and  $[\text{Sm}(\text{NO}_3)_3(\text{Ph}_3\text{QO})_2(\text{EtOH})] \cdot \text{acetone}$  ( $\text{Q} = \text{P}, \text{As}$ ) have all been shown to have nine-coordinate samarium.

### 4.6 The Coordination Chemistry of the +2 and +4 States

These areas have remained relatively undeveloped until recently; with increasing emphasis on the use of nonaqueous solvents, many discoveries in the (+2) state for Eu, Sm, and Yb in particular probably remain to be made.



### 4.6.1 The (+2) State

Solutions of  $\text{Eu}^{3+}(\text{aq})$  are reduced by zinc to  $\text{Eu}^{2+}(\text{aq})$ ; this can be precipitated as the sulfate, affording a separation from the other  $\text{Ln}^{3+}(\text{aq})$  ions, which were not reduced under these conditions, used for many years in the purification of the lanthanides. In general the solubilities of the 'inorganic' compounds of the  $\text{Ln}^{2+}$  ions resemble those of the corresponding compounds of the alkaline earth metals (insoluble sulfate, carbonate, hydroxide, oxalate). Electrolytic reduction is one of a number of methods that can be used to generate solutions of  $\text{Eu}^{2+}$ ,  $\text{Sm}^{2+}$ , and  $\text{Yb}^{2+}$  ions; aqueous solutions of  $\text{Sm}^{2+}$  and  $\text{Yb}^{2+}$  tend to be short-lived and oxygen-sensitive in particular. These and other divalent lanthanides can be stabilized by the use of nonaqueous solvents such as HMPA and THF, in which they have characteristic colours, different and deeper than those in the isoelectronic  $\text{Ln}^{3+}$  ions on account of the decreased term separations in the divalent ions (typically,  $\text{Eu}^{2+}$  pale yellow;  $\text{Sm}^{2+}$  red;  $\text{Yb}^{2+}$  green-yellow;  $\text{Tm}^{2+}$  green;  $\text{Dy}^{2+}$  brown;  $\text{Nd}^{2+}$  red).

A significant number of complexes are now known, including  $\text{SmCl}_2(\text{thf})_5$  and  $\text{EuI}_2(\text{thf})_5$  (pentagonal bipyramidal); polymeric  $[\text{SmCl}_2(\text{Bu}^t\text{CN})_2]_\infty$  (six coordinate);  $\text{LnI}_2(N\text{-methylimidazole})_4$  ( $\text{Ln} = \text{Sm}, \text{Eu}$ );  $\text{EuCl}_2(\text{phen})_2$  and  $\text{EuCl}_2(\text{terpy})$ ; *trans*- $\text{EuI}_2(\text{thf})_4$ ;  $[\text{Yb}(\text{hmpa})_4(\text{thf})_2]\text{I}_2$ ,  $[\text{Sm}(\text{hmpa})_6]\text{I}_2$ ,  $[\text{Sm}(\text{hmpa})_4]\text{I}_2$  and the eight-coordinate  $[\text{SmI}_2\{\text{O}(\text{C}_2\text{H}_4\text{OME})_2\}]$  (the latter existing as *cis* and *trans* isomers). Compounds of lanthanides with an accessible  $\text{Ln}^{2+}$  ion yet previously unknown coordination chemistry are starting to be made, such as  $[\text{LnI}_2(\text{dme})_3]$  and  $[\text{LnI}_2(\text{thf})_5]$  ( $\text{Ln} = \text{Nd}, \text{Dy}$ ), made by reaction of Nd and Dy with  $\text{I}_2$  at 1500 °C, followed by dissolution of the product in the appropriate ligand.  $[\text{TmI}_2(\text{dme})_3]$  has seven-coordinate thulium, with one monodentate dimethoxyethane; the samarium analogue, which contains a larger metal ion, has eight coordination.

The bis(silylamide) complexes  $\text{Ln}[\text{N}(\text{SiMe}_3)_2]_2$  ( $\text{Ln} = \text{Eu}, \text{Yb}$ ) are well characterized; because of the bulky ligands, these tend to exhibit three and four coordination, much as for the corresponding compounds in the +3 oxidation state. Thus  $\text{Yb}[\text{N}(\text{SiMe}_3)_2]_2$  is a dimer with two bridging alkylamides, and the  $[\text{Eu}\{\text{N}(\text{SiMe}_3)_2\}_2]^-$  ion is trigonal planar (unlike the  $\text{Eu}^{\text{III}}$  analogue). These compounds form adducts with monomeric structures;  $\text{M}[\text{N}(\text{SiMe}_3)_2]_2\text{L}_2$  ( $\text{M} = \text{Eu}, \text{Yb}$ ; L, e.g.,  $\text{PBu}_3$ , THF;  $\text{L}_2 = \text{dmpe}$ ) are four-coordinate, and  $\text{Eu}[\text{N}(\text{SiMe}_3)_2]_2(\text{glyme})_2$  is six-coordinate.

There is a developing chemistry with alkoxide and aryloxide as well as amide ligands, together with organometallics. To give some examples from ytterbium(II) aryloxides,  $\text{Yb}(\text{Odpp})_2(\text{thf})_3$  (Odpp = 2,6-diphenylphenoxide) is trigonal bipyramidal, whilst with the very bulky 2,6-di-*tert*-butyl-4-methylphenoxy (Odtb) ligand the adduct  $\text{Yb}(\text{Odtb})_2(\text{thf})_2$  is tetrahedral whilst  $\text{Yb}(\text{Odtb})_2(\text{thf})_3$  is five-coordinate square pyramidal. Among compounds with the heavier Group VI (16) donor atoms,  $\text{Yb}(\text{SAr})_2(\text{MeOCH}_2\text{CH}_2\text{OMe})_2$  and  $\text{Ln}(\text{Qmes})_2(\text{thf})_n$  ( $\text{Ln} = \text{Yb}, \text{Sm}, \text{Eu}$ ; Q = Se, Te; mes = 2,4,6-trimethylphenyl) are examples. The most striking organometallics are the two-coordinate alkyls  $[\text{Ln}[\text{C}(\text{SiMe}_3)_3]_2]$  ( $\text{Ln} = \text{Yb}, \text{Eu}$ ), the aryls  $\text{LnPh}_2(\text{thf})_n$  ( $\text{Ln} = \text{Eu}, \text{Yb}$ ), with as-yet unknown structures,  $\text{Yb}(\text{C}_6\text{F}_5)_2(\text{thf})_4$  of unknown structure, and  $\text{Eu}(\text{C}_6\text{F}_5)_2(\text{thf})_5$  having a pentagonal bipyramidal structure, with all thf equatorial. The synthesis has also been reported of tetrahedral  $[\text{Eu}(\text{dpp})_2(\text{thf})_2]$  (dpp = 2,6-diphenylphenyl). Much of this work is very recent, though cyclopentadienyl-type systems have long been known in the (+2) state. Organometallics are discussed in more detail in Chapter 6.

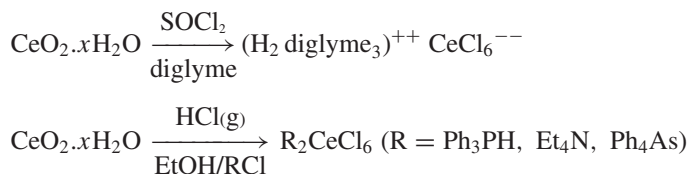


### 4.6.2 The (+4) State

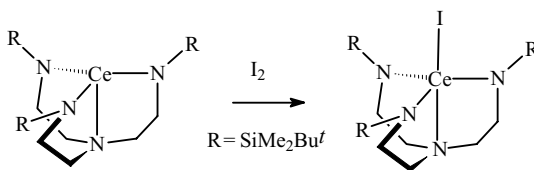
Cerium is the only lanthanide with an extensive chemistry in this oxidation state. The cerium (+4) aqua ion, obtained by acid dissolution of  $\text{CeO}_2$ , is thermodynamically unstable but kinetically stable; the anion sensitivity of the reduction potentials ( $E = 1.61$  V in 1M  $\text{HNO}_3$ ; 1.44 V in 1M  $\text{H}_2\text{SO}_4$ ; and 1.70 V in 1M  $\text{HClO}_4$ ) indicates that complexes are involved rather than just a simple aqua ion. Salts are known, including  $\text{CeSO}_4 \cdot 4\text{H}_2\text{O}$  and  $\text{Ce}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ ; the latter probably contains 11-coordinate  $[\text{Ce}(\text{NO}_3)_4 \cdot (\text{H}_2\text{O})_3]$  molecules, like the thorium analogue. Cerium is 10 coordinate in the  $[\text{Ce}(\text{CO}_3)_5]^{6-}$  ion and 12 coordinate in  $[\text{Ce}(\text{NO}_3)_6]^{2-}$ , the ion found in the familiar orange-red salt  $(\text{NH}_4)_2[\text{Ce}(\text{NO}_3)_6]$ , widely used as an oxidizing agent in organic chemistry and in titrimetric analysis.

Cerium(IV) halide complexes include  $(\text{NH}_4)_4[\text{CeF}_8]$  (square antiprismatic) and  $(\text{NH}_4)_3\text{CeF}_7 \cdot (\text{H}_2\text{O})$  (dimeric, with dodecahedral coordination in the  $\text{Ce}_2\text{F}_{12}^{6-}$  ions) which are prepared by crystallization; heating the former decomposes it to  $(\text{NH}_4)_2\text{CeF}_6$ , which contains infinite  $(\text{CeF}_6^{2-})_\infty$  chains. Heating an  $\text{MCl}/\text{CeO}_2$  mixture in fluorine gives alkali metal salts  $\text{M}_2\text{CeF}_6$  and  $\text{M}_3\text{CeF}_7$  ( $\text{M} = \text{Na}-\text{Cs}$ ); unlike the ammonium salts, these are water-sensitive and cannot be made by wet methods. The ammonium salts may be more stable because hydrogen bonding between the ammonium ions and fluoride ions could contribute to a higher lattice energy.

Although the binary chloride does not exist, a number of hexachloro salts have been made:



These may be converted into the analogous violet, moisture-sensitive salts of the  $[\text{CeBr}_6]^{2-}$  ion on treatment with gaseous  $\text{HBr}$ . No salts of the  $[\text{CeI}_6]^{2-}$  ion have been reported, presumably for redox reasons, though a compound with a  $\text{Ce}^{(\text{IV})}-\text{I}$  bond has been made (Figure 4.13).



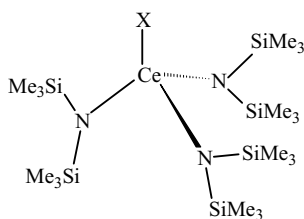
**Figure 4.13**

A compound with a  $\text{Ce}(\text{I})-\text{I}$  bond.

The four nitrogen atoms are good donors and reduce the effective charge on the cerium, affecting its reduction potential.

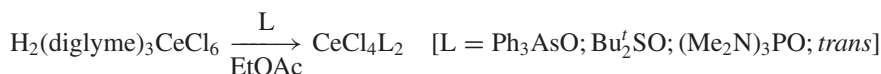
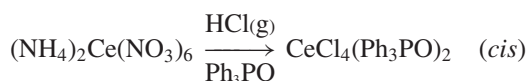
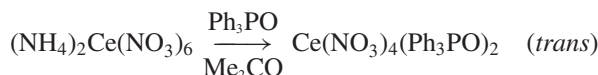
$[\text{Ce}\{\text{N}(\text{SiMe}_3)_2\}_3]$  is an obvious choice of starting material for the synthesis of other  $\text{Ce}^{\text{IV}}$  amides, but oxidation with  $\text{Cl}_2$  or  $\text{Br}_2$  was not successful; however, use of  $\text{TeCl}_4$  oxidant led to  $[\text{Ce}(\text{Cl})\{\text{N}(\text{SiMe}_3)_2\}_3]$  and similarly  $\text{Ph}_3\text{PBr}_2$  afforded  $[\text{Ce}(\text{Br})\{\text{N}(\text{SiMe}_3)_2\}_3]$  (Figure 4.14). The corresponding iodo compound has not (yet) been synthesized.

A number of neutral complexes of O-donor Lewis bases have been made, such as ten-coordinate *trans*- $\text{Ce}(\text{NO}_3)_4(\text{Ph}_3\text{PO})_2$  and octahedral  $\text{CeCl}_4\text{L}_2$  [ $\text{L} = \text{Ph}_3\text{PO}, \text{Ph}_3\text{AsO}$ ,

**Figure 4.14**

X = Br, Cl

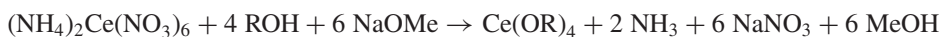
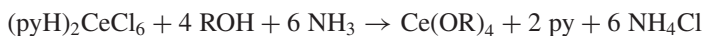
(Me<sub>2</sub>N)<sub>3</sub>PO, Bu'<sub>2</sub>SO, (H<sub>2</sub>N)<sub>2</sub>CO]. They are prepared thus:



The CeCl<sub>4</sub>(Ph<sub>3</sub>PO)<sub>2</sub> complex is *cis*, like the uranium analogue, whilst an X-ray diffraction study of CeCl<sub>4</sub>[(Me<sub>2</sub>N)<sub>3</sub>PO]<sub>2</sub> (*trans*) showed a close structural correspondence to the corresponding U<sup>IV</sup> compound.

Ce(R<sup>1</sup>.CO.CH.CO.R<sup>2</sup>)<sub>3</sub> are readily oxidized (O<sub>2</sub>) to Ce(R<sup>1</sup>.CO.CH.CO.R<sup>2</sup>)<sub>4</sub>, such as Ce(acac)<sub>4</sub> (R<sup>1</sup> = R<sup>2</sup> = Me), Ce(dbm)<sub>4</sub> (R<sup>1</sup> = R<sup>2</sup> = Ph), and Ce(tmhd)<sub>4</sub> (R<sup>1</sup> = R<sup>2</sup> = Me<sub>3</sub>C), generally found to have square antiprismatic structures, though Ce(tmhd)<sub>4</sub> is closer to dodecahedral. These are volatile dark red solids that are soluble in solvents such as benzene and chloroform; they are volatile, with vapour pressures high enough for Metal Organic Chemical Vapour Deposition (MOCVD) use, whilst they have also been studied as possible alternatives to lead compounds for petrol additives.

Another feature of the chemistry of cerium (IV) is the alkoxides.



Most are involatile oligomers, though the isopropoxide is volatile *in vacuo* below 200 °C {its bis(propan-2-ol) adduct [Ce<sub>2</sub>(OPr<sup>i</sup>)<sub>8</sub>(Pr<sup>i</sup>OH)<sub>2</sub>] is a dimer with 6-coordinate cerium} and it can achieve coordinative saturation in adducts like [Ce(OR)<sub>4</sub>(thf)<sub>2</sub>] (R = CMe<sub>3</sub>, SiPh<sub>3</sub>) and [Ce(OCMe<sub>3</sub>)<sub>6</sub>]<sup>2-</sup>. Heating [Ce<sub>2</sub>(OPr<sup>i</sup>)<sub>8</sub>(Pr<sup>i</sup>OH)<sub>2</sub>] gives [Ce<sub>4</sub>O(OPr<sup>i</sup>)<sub>14</sub>], which is [Ce<sub>4</sub>(μ<sub>4</sub>-O)(μ<sub>3</sub>-OPr<sup>i</sup>)<sub>2</sub>(μ-OPr<sup>i</sup>)<sub>8</sub>(OPr<sup>i</sup>)<sub>4</sub>], an oxo-centred cluster similar to those found with Ln<sup>III</sup> alkoxides.

Cerium also forms genuine bis(porphyrin) and bis(phthalocyanine) complexes with the metal in the (+4) oxidation state.

Although other (+4) oxides exist in the form of PrO<sub>2</sub> and TbO<sub>2</sub>, no other (+4) aqua ions are known; these oxides oxidize acids on dissolution, forming the M<sup>3+</sup> (aq) ions. Alkali metal fluoro-complexes Cs<sub>3</sub>LnF<sub>7</sub> (Ln = Pr, Nd, Tb, Dy) and M<sub>2</sub>LnF<sub>6</sub> (M = Na–Cs, Ln = Tb, Pr) are known for four other lanthanides; as with Ce<sup>IV</sup>, they have to be made by dry methods, by fluorination of Cs<sub>3</sub>LnCl<sub>6</sub> using XeF<sub>2</sub> or MCl/Ln<sub>2</sub>O<sub>3</sub> mixtures using F<sub>2</sub>.

**Question 4.1** Study the data in Tables 4.1 and 4.2 (above). Plot a graph of  $\log \beta$  against atomic number for complex formation with  $\text{EDTA}^{4-}$ . Deduce and explain the patterns in behaviour for the lanthanides; compare the values of the stability constants for EDTA and fluoride complexes.

**Answer 4.1** The values for  $\text{Lu}^{3+}$  are greater than those for  $\text{La}^{3+}$  as the smaller  $\text{Lu}^{3+}$  ion has a greater charge density and stronger electrostatic attraction for a ligand. Values for multidentate ligands are greater than those for monodentate ligands, partly because of entropy factors and also because once one end of a ligand is attached, there is a higher chance of the other donor atoms attaching themselves.

**Question 4.2** Suggest why the acetates of the lanthanides do not adopt structures with  $\text{M}_3\text{O}$  cores as found for many carboxylates of trivalent transition metals (e.g. Cr, Mn, Fe).

**Answer 4.2** A Molecular Orbital scheme for species such as  $[\text{M}_3\text{O}(\text{OAc})_6]^+$  has d-p  $\pi$ -bonding involving the metals and the central oxygen atom. Lanthanide f orbitals are buried too deeply to permit such overlap.

**Question 4.3** A summary of structure types in the lanthanide chloride complexes of THF is given in Table 4.3 (data based upon G.B. Deacon, T. Feng, P.C. Junk, B.W. Skelton, A.N. Sobolev and A.H. White, *Aust. J. Chem.*, 1998, **51**, 75).

Use the list of structure types to work out the coordination number of the lanthanide for each compound. Plot a scatter graph of Average coordination number (y axis) against Atomic number (x axis) and comment.

**Answer 4.3** There is a decrease in CN as the ionic radius decreases. The isolation of a number of complexes for some of the metal ions may reflect other factors such as the solubility of the complexes and the stoichiometry of the reaction mixtures.

**Question 4.4** Why do  $\text{Ln}(\text{acac})_3$  form Lewis base adducts, when transition metal analogues  $\text{M}(\text{acac})_3$  (M, e.g., Cr, Fe, Co) do not?

**Answer 4.4** The lanthanides are larger than transition metals and therefore  $\text{Ln}(\text{acac})_3$  are coordinatively unsaturated.

**Question 4.5** Why is a nine-coordinate  $\text{Eu}(\text{dpm})_3(\text{terpy})$  known and not (for example)  $\text{Eu}(\text{dpm})_3(\text{H}_2\text{O})_3$ ?

**Answer 4.5** In terpyridyl, the three donor atoms are part of one molecule and take up less space than three individual molecules, even small ones.

**Table 4.3** Lanthanide chloride complexes with THF

Structure types characterized													
La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
1	2	2	2,3	3	3	3,4	4	4	4	4	4	5,6	6

Description of types:

1.  $\text{La}(\text{thf})_2(\mu\text{-Cl})_3\text{Ln}(\text{thf})_2(\mu\text{-Cl})_3\text{La} \dots$
2.  $\text{LaCl}(\text{thf})_2(\mu\text{-Cl})_2\text{LnCl}(\text{thf})_2(\mu\text{-Cl})_2\text{La} \dots$
3.  $[\text{LnCl}_3(\text{thf})_4]$ .
4.  $[\text{LnCl}_2(\text{thf})_5]^+ [\text{LnCl}_4(\text{thf})_2]^-$ .
5.  $[\text{Cl}_2(\text{thf})_2\text{Ln}(\mu\text{-Cl})_2\text{Ln}(\text{thf})_2\text{Cl}_2]$ .
6.  $[\text{LnCl}_3(\text{thf})_3]$ .

**Question 4.6** Chinese workers have reported compounds with the formula  $\text{Ln}(\text{acac})_3(\text{Ph}_3\text{PO})_3$  (Ln, e.g., Nd, Eu, Ho). Comment on this.

**Answer 4.6** Even though acac is the least bulky  $\beta$ -diketonate ligand, it would be surprising if all the  $\text{Ph}_3\text{PO}$  groups were coordinated (recall that  $\text{Ph}_3\text{PO}$  is sterically more demanding than water as a ligand). Ultimately, only X-ray diffraction studies can settle this.

**Question 4.7** Why in general does nitrate coordinate to the metal in crown ether complexes but chloride does not?

**Answer 4.7** Nitrate has a small bite angle and takes up little more space in the coordination sphere than a chloride ion; forming two  $\text{Ln}-\text{O}$  bonds is energetically more favourable than forming one  $\text{Ln}-\text{Cl}$  bond and can outweigh the considerable  $\text{Ln}^{3+}-\text{OH}_2$  bond energy.

**Question 4.8** Lanthanide thiocyanate complexes are N-bonded, not S-bonded. Why is this expected?

**Answer 4.8**  $\text{Ln}^{3+}$  ions are ‘hard’ acids, which prefer to bond to ‘hard’ bases. Sulfur is a ‘softer’ base than nitrogen.

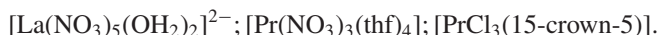
**Question 4.9** Explain why europium nitrate forms a 1:1 complex  $[\text{Eu}(\text{terpy})(\text{NO}_3)_3(\text{H}_2\text{O})]$  but europium perchlorate forms a 3:1 complex  $[\text{Eu}(\text{terpy})_3](\text{ClO}_4)_3$ .

**Answer 4.9** Perchlorate is a weakly coordinating anion, so does not compete with terpyridyl; nitrate has reasonably strong coordinating tendencies, usually as a bidentate ligand, and does compete with terpy. Three nitrate groups will occupy six coordinating positions, leaving room for only one terpy.

**Question 4.10** Why might  $\text{Ce}(\text{R}^1\text{COCH(R}^2\text{)})_4$  be expected to be a better MOCVD precursor and petrol additive than  $\text{Ce}(\text{R}^1\text{COCH(R}^2\text{)})_3$ ?

**Answer 4.10**  $\text{Ln}^{\text{III}}$   $\beta$ -diketonates are often coordinatively unsaturated (Section 4.3.4) and tend to polymerize. The molecular nature of the  $\text{Ce}^{\text{IV}}$  compounds should confer greater volatility, as well as solubility in nonpolar solvents (e.g. petrol). The  $\text{Ce}^{\text{IV}}$  oxidation state may also assist the oxidation process.

**Question 4.11** Suggest coordination numbers for the metal in each of the following:



**Answer 4.11** 12, 10, 8 respectively.

**Question 4.12** Suggest geometries for (a)  $[\text{Eu}[(\text{N}(\text{SiMe}_3)_2)_3]^-]$ ; (b)  $[\text{Yb}[(\text{N}(\text{SiMe}_3)_2)_2(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)]]$ ; (c)  $\text{Ln}[(\text{N}(\text{SiMe}_3)_2)_3(\text{NCMe})_2]$ ; (d)  $(\text{Me}_4\text{N})_3[\text{Ln}(\text{NCS})_7]$ ; (e)  $[\text{Li}(\text{tmed})_2]^+ [\text{LuBu}_4']^-$ .

**Answer 4.12** (a) Trigonal/triangular; (b) tetrahedral; (c) trigonal bipyramid with axial nitriles; (d) capped octahedron/trigonal prism; (e) tetrahedral.

**Question 4.13** Comment on the oxidation state of  $[\text{Ce}_4\text{O}(\text{OPr}^i)_{14}]$ .

**Answer 4.13** Taking O as  $-2$  and  $\text{OPr}^i$  as  $-1$  leads to an assignment of the oxidation state of Ce as  $+4$ , further illustration of the stability of this state, when a redox reaction might have been expected.

**Question 4.14**  $\text{Ln}[\text{N}(\text{SiMe}_3)_2]_3$  are pentane-soluble and sublime in vacuum at 100 °C, whereas the much lighter  $\text{LnCl}_3$  have high melting and boiling points and do not dissolve in organic solvents. Explain why.

**Answer 4.14**  $\text{LnCl}_3$  have giant ionic lattice structures, because of the relatively small size of the chloride ion. The nonpolar pentane cannot break up the ionic lattice to dissolve it. In contrast, the bulky silylamide ligands shield the metal ion, preventing oligomerization and also presenting an ‘organic exterior’ to the solvent pentane. The presence of weak, essentially van der Waals’-type intermolecular forces means that little energy is needed to vapourize the amides and little energy change occurs on dissolution in a nonpolar solvent.

**Question 4.15** Three routes for the synthesis of alkoxides involve (i) the reaction of  $\text{LnCl}_3$  with an alkali metal alkoxide, (ii) reaction of an alkali metal with an alcohol, (iii) the reaction of a silylamide  $[\text{Ln}\{\text{N}(\text{SiMe}_3)_2\}_3]$  with an alcohol. What are the advantages and disadvantages of each?

**Answer 4.15** (i) The chemicals are readily available. The chloride is fairly insoluble in organic solvents and it is possible that chlorine is retained in the product. (ii) There is no need to make the alkali metal alkoxide, as the alcohol is the starting material. The metal may need careful cleaning and there may be the need for heating and a catalyst. One product is a gas. (iii) The lanthanide silylamide has to be prepared first. Because of the bulky nature of the ligand, it may be inert to substitution, but there are no problems with chloride retention and the reaction should be clean.

**Question 4.16** Lanthanide alkoxide clusters do not contain metal–metal bonds. Transition metal carbonyl clusters frequently do. Comment.

**Answer 4.16** Transition metal carbonyls have transition metals in low oxidation states where d orbitals can overlap well. f orbital involvement in bonding in lanthanide compounds is minimal and the high oxidation state will contract the orbitals even further.

**Question 4.17** Given the  $\text{Zn}^{2+}/\text{Zn}$  reduction potential of  $-0.76\text{ V}$ , and using values for  $\text{Ln}^{3+}/\text{Ln}^{2+}$  given in Table 2.7, explain why this can be used to separate Eu from other lanthanides that form  $\text{Ln}^{2+}$  ions.

**Answer 4.17** Since  $E = -0.76\text{ V}$  for  $\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn}$ , it will reduce  $\text{Eu}^{3+}$  to  $\text{Eu}^{2+}$ ; since the reduction potential for  $\text{Eu}^{3+} + \text{e}^- \rightarrow \text{Eu}^{2+}$  is  $-0.34\text{ V}$ , the potential for the reaction  $2\text{Eu}^{3+} + \text{Zn} \rightarrow 2\text{Eu}^{2+} + \text{Zn}^{2+}$  is  $+0.42\text{ V}$ , and the reduction is feasible. However, the reduction potentials for the other  $\text{Ln}^{3+}$  ions are all more negative than that for  $\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn}$ ; for the next most easily reduced lanthanide (III) ion, ytterbium,  $E = -1.05\text{ V}$  for  $\text{Yb}^{3+} + \text{e}^- \rightarrow \text{Yb}^{2+}$ , and thus zinc will not reduce  $\text{Yb}^{3+}$  to  $\text{Yb}^{2+}$ .

# 5 Electronic and Magnetic Properties of the Lanthanides

By the end of this chapter you should be able to:

- know how to use Hund's rules to work out the ground state of lanthanide ions;
- calculate the magnetic moments for these ions, given the appropriate formula;
- understand why spin-only values for the moments are inadequate;
- state why the magnetic moments measured for  $\text{Sm}^{3+}$  and  $\text{Eu}^{3+}$  compounds differ from these predictions;
- appreciate why electronic (excitation) spectra show little dependence on compound, for a particular metal ion;
- be aware of the existence of hypersensitive transitions;
- interpret electronic spectra of compounds in terms of energy level diagrams;
- understand the causes of fluorescence in compounds of the lanthanides, particularly compounds of  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$ ;
- interpret the fluorescence spectra of  $\text{Eu}^{3+}$  compounds in terms of the site symmetry;
- understand the principles involved in applications, including  $\text{Nd}^{3+}$  in lasers, and the use of lanthanides in lighting and TV tubes;
- explain the use of lanthanide complexes as MRI agents and NMR shift reagents.

## 5.1 Magnetic and Spectroscopic Properties of the $\text{Ln}^{3+}$ Ions

These may be accounted for using the Russell–Saunders coupling scheme in which the electron spins are coupled together separately from the coupling of the orbital angular momenta of the electrons, and the orbital moment is unquenched. The ground state for a given lanthanide ion is unaffected by the ligands bound to it – and thus crystal field splittings are weak – because of the shielding of the 4f electrons by the filled 5s and 5p orbitals.

The spins of the individual electrons(s) are coupled together (added vectorially) to give the spin quantum number for the ion ( $S$ ). The orbital angular momenta ( $l$ ) of the individual electrons are coupled similarly.

For an f electron,  $l = 3$ , so that the magnetic quantum number  $m_l$  can have any one of the seven integral values between +3 and –3. Vectorial addition of the  $m_l$ -values for the f electrons for the multi-electron ion affords  $L$ , the total orbital angular momentum quantum number:

There is a weaker coupling, spin–orbit coupling, between  $S$  and  $L$ .

$L$	0	1	2	3	4	5	6	7
State symbol	S	P	D	F	G	H	I	K

**Figure 5.1**

State symbols for different values of  $L$ .

$m_l$	3	2	1	0	-1	-2	-3
	↑	↑	↑	↑	↑		

**Figure 5.2**

Box diagram for  $\text{Sm}^{3+}$ .

Vector addition of  $L$  and  $S$  affords the resulting quantum number,  $J$ .  $J$  can have values of  $(L + S)$ ,  $(L + S) - 1$ ; . . . . .  $(L - S)$ . To take an example, if  $L = 6$  and  $S = 2$ ,  $J$ -values of 8, 7, 6, 5, and 4 are possible.

For any ion, a number of electronic states are possible. The ground state can be determined using Hund's rules (in this order):

1. The spin multiplicity  $(2S + 1)$  is as high as possible.
2. If there is more than one term with the same spin multiplicity, the term with the highest  $L$ -value is the ground state.
3. For a shell less than half-filled,  $J$  for the ground state takes the lowest possible value; for a shell more than half-filled,  $J$  for the ground state is the highest possible.

To give an example, working out the term symbol for the ground state of  $\text{Sm}^{3+}$  ( $f^5$ ) First complete a 'box diagram', representing orbitals by boxes (7 boxes for 7  $f$  orbitals) and electrons by arrows (Figure 5.2). Put electrons in separate orbitals when the shell is less than half-filled, i.e. choosing the maximum number of unpaired electrons, and choosing to maximize the values of  $m_l$  to give the highest  $L$ -value (check Hund's rule 2).

So  $S = \sum m_s = 5/2$ , therefore  $2S + 1 = 2(5/2) + 1 = 6$ .

$L = \sum m_l = +3 + 2 + 1 + 0 - 1 = +5$ , so it is an H state.

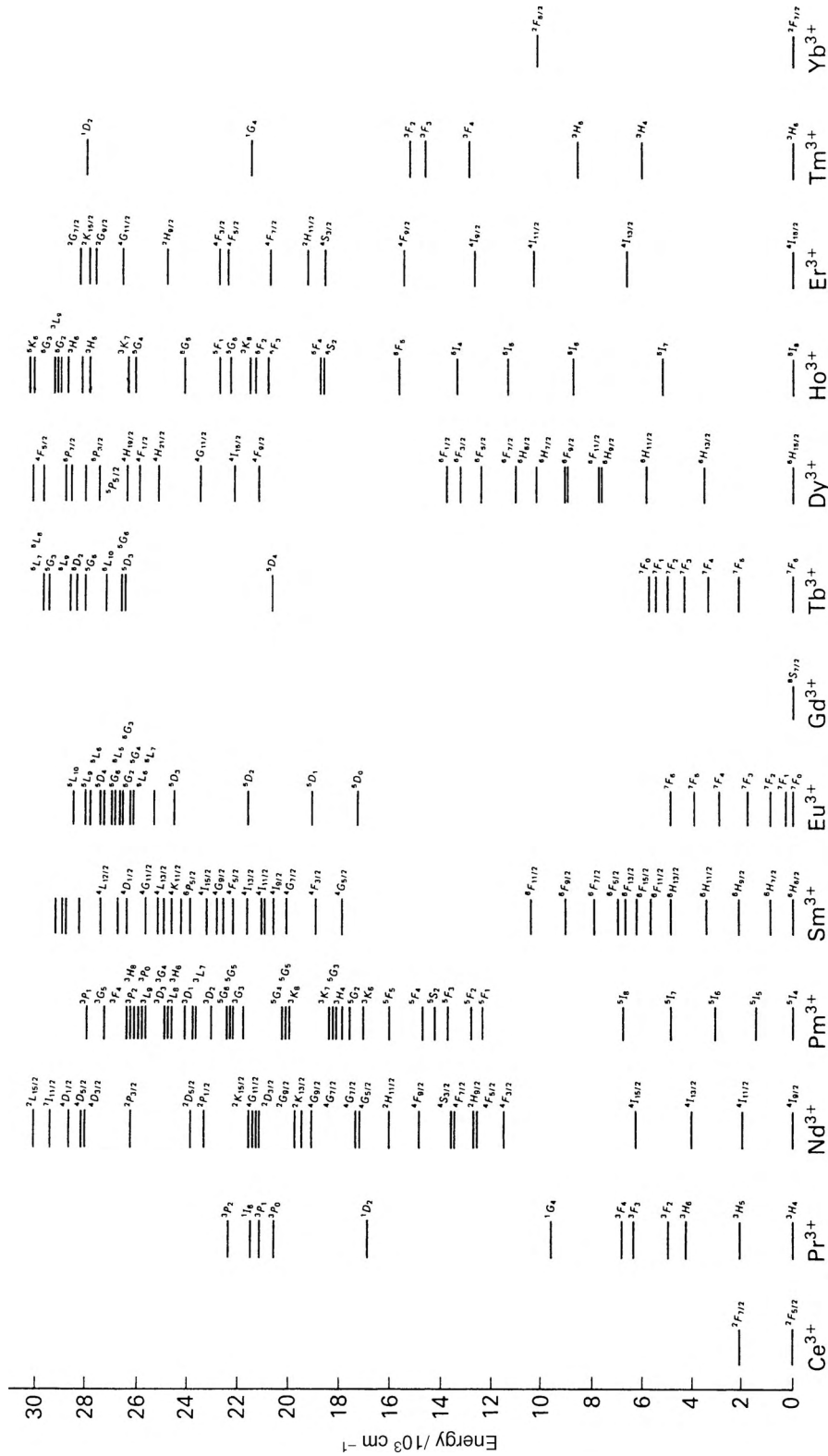
$J$  can have the values of  $(L + S)$ ;  $(L + S) - 1$ ;  $(L + S) - 2$ ; . . . . .;  $(L - S)$ , so here  $J = (5 + 5/2)$ ;  $(5 + 5/2) - 1$ ;  $(5 + 5/2) - 2$  . . . . .  $(5 - 5/2) = 15/2$ ;  $13/2$ ;  $11/2$ ;  $9/2$ ;  $7/2$ ;  $5/2$ .

Since the shell is less than half-filled, the state with the lowest  $J$ -value is the ground state (Hund's third rule), so this is  $J = 5/2$ .

The term symbol for the ground state of  $\text{Sm}^{3+}$  is thus  $^6\text{H}_{5/2}$

## 5.2 Magnetic Properties of the $\text{Ln}^{3+}$ Ions

With the exception of  $\text{La}^{3+}$  and  $\text{Lu}^{3+}$  (and of course  $\text{Y}^{3+}$ ) the  $\text{Ln}^{3+}$  ions all contain unpaired electrons and are paramagnetic. Their magnetic properties are determined entirely by the ground state (with two exceptions we shall encounter), as the excited states are so well separated from the ground state (owing to spin-orbit coupling; see Figure 5.3) and are thus thermally inaccessible.



**Figure 5.3**

Energy levels of the  $\text{Ln}^{3+}$  ions [from S. Hüfner, in S.P. Sinha (ed.), *Systematics and Properties of the Lanthanides*, Reidel, Dordrecht, 1983; reproduced by permission of the publisher and author].



The magnetic moment of the  $\text{Ln}^{3+}$  ions is essentially independent of environment, so that one cannot distinguish between coordination geometries as is sometimes possible for transition metals – in the case of octahedral and tetrahedral  $\text{Co}^{2+}$  complexes, for example. The moments are given by the equation:

$$\mu_{\text{eff}} = g_J \sqrt{J(J+1)}$$

where the Landé  $g$ -factor is defined by:

$$g_J = [S(S+1) - L(L+1) + 3J(J+1)]/2J(J+1); \text{ this may also be written}$$

$$g_J = 3/2 + [S(S+1) - L(L+1)]/2J(J+1)$$

This differs from the familiar  $\mu_{\text{eff}} = \sqrt{n(n+2)}$  formula, where  $n$  is the number of unpaired electrons, [or  $\sqrt{4S(S+1)}$ , spin-only formula], often applicable to the  $3d^n$  transition metal ions, as in the latter case the orbital contribution to the moment is quenched by the interaction of the metal's  $3d$  orbitals with the ligands.

The magnetic moments in the second half of the series are greater than the moments in the first half, as  $J = L + S$  for a shell greater than half-filled and  $J = L - S$  for a less than half-filled shell.

**Example:** Calculate the magnetic moment for a complex of  $\text{Ho}^{3+}$ , such as  $\text{Ho}(\text{phen})_2(\text{NO}_3)_3$ .

The ground state is  $^5\text{I}_8$  ( $^{2S+1}L_J$ ), since  $2S+1=5$ ,  $S=2$ ;  $L=6$  (I state);  $J=8$ .  $g_J$  must first be calculated;  $g_J = 3/2 + [S(S+1) - L(L+1)]/2J(J+1)$

Substituting,  $g_J = 3/2 + [2(2+1) - 6(6+1)]/2 \times 8(8+1) = 3/2 - 36/144$ , so  $g_J = 5/4$ .

Now substitute in  $\mu_{\text{eff}} = g_J \sqrt{J(J+1)}$ ;  $\mu_{\text{eff}} = 5/4 \sqrt{8(8+1)} = 10.60 \mu_B$

The strength of spin-orbit coupling means that the ground state is well separated from excited states, except for  $\text{Sm}^{3+}$  and  $\text{Eu}^{3+}$ , where contributions from low-lying paramagnetic excited states (see Figure 5.3) contribute to the magnetic moment. Thus, if the magnetic properties of the  $\text{Eu}^{3+}$  ion were solely determined by the  $^7\text{F}_0$  ground state, its compounds would be diamagnetic, whereas contributions from thermally accessible levels such as  $^7\text{F}_1$  and  $^7\text{F}_2$  [using a Boltzmann factor of  $\exp(-\Delta E/kT)$ ] lead to the observed room-temperature magnetic moments in the region of  $3.5 \mu_B$ . Similarly, in the case of  $\text{Sm}^{3+}$ , thermal population of the  $^6\text{H}_{7/2}$  state leads to moments around  $1.6 \mu_B$ , rather than the value of  $0.845 \mu_B$  that would be expected if just the  $^6\text{H}_{5/2}$  ground state were responsible.

### 5.2.1 Adiabatic Demagnetization

This application of the high magnetic moments of lanthanide complexes is a process by which the removal of a magnetic field from certain materials lowers their temperature; it was proposed independently in 1926–1927 by Peter Debye and William Francis Giauque (Giauque won the Nobel prize for Chemistry in 1949 for his low-temperature work). It is applied particularly to cooling an extremely cold material at  $\sim 1$  K to much lower temperatures, perhaps as low as  $0.0015$  K. An Adiabatic Demagnetization Refrigerator uses certain highly paramagnetic lanthanide salts [e.g.  $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ ] immersed in a bath of liquid helium; the lanthanide ions in the second half of the series have higher magnetic moments (see Table 5.1) so compounds of  $\text{Gd}^{3+}$  and  $\text{Dy}^{3+}$  tend to be used.

**Table 5.1** Magnetic Moments of  $\text{Ln}^{3+}$  ions at room temperature

	$f^n$	Ground term	Predicted $\mu_{\text{eff}} (\mu_{\text{B}})$	$\mu_{\text{eff}}$ $\text{M(phen)}_2(\text{NO}_3)_3 (\mu_{\text{B}})$
La	0	$^1\text{S}_0$	0.00	0
Ce	1	$^2\text{F}_{5/2}$	2.54	2.46
Pr	2	$^3\text{H}_4$	3.58	3.48
Nd	3	$^4\text{I}_{9/2}$	3.68	3.44
Pm	4	$^5\text{I}_4$	2.83	
Sm	5	$^6\text{H}_{5/2}$	0.85	1.64
Eu	6	$^7\text{F}_0$	0.00	3.36
Gd	7	$^8\text{S}_{7/2}$	7.94	7.97
Tb	8	$^7\text{F}_6$	9.72	9.81
Dy	9	$^6\text{H}_{15/2}$	10.63	10.6
Ho	10	$^5\text{I}_8$	10.60	10.7
Er	11	$^4\text{I}_{15/2}$	9.59	9.46
Tm	12	$^3\text{H}_6$	7.57	7.51
Yb	13	$^2\text{F}_{7/2}$	4.53	4.47
Lu	14	$^1\text{S}_0$	0.00	0

If the paramagnetic substance is placed in a strong external magnetic field, the magnetic dipoles tend to align with the field. This is an exothermic process, as ‘aligned’ is the lowest energy state, and unaligned dipoles need to lose energy to achieve the lowest state. The heat energy released is removed by the external coolant, and the magnetic material (and its surroundings) cool back to their original temperature (say 1 K). Thermal contact between the material and the liquid helium bath is now broken (a ‘heat switch’ is turned off) and the magnetic field is turned off. The magnetic dipoles tend to randomize now, absorbing thermal energy from the magnetic material, which cools (along with its immediate surroundings), producing the cooling in the sample.

## 5.3 Energy Level Diagrams for the Lanthanide Ions, and their Electronic Spectra

Energy level diagrams for all the  $\text{Ln}^{3+}$  ions are shown in Figure 5.3.

These are based on theoretical predictions, coupled with experimental results. Accurate values have been determined in many experimental situations, such as halide lattices like  $\text{LnF}_3$ , which closely resemble those of the gaseous ions. In the lanthanide ions, the filled ‘outer’ 5s and 5p orbitals efficiently shield the 4f electrons from surrounding ligands, with the result that crystal field splittings are of the order of  $100 \text{ cm}^{-1}$ . The weak crystal field splittings can thus be treated as a perturbation upon the free-ion levels; in contrast, of course, in the 3d metals, CF splittings are large and L–S coupling is weak. A consequence of the lack of CF effects in the lanthanides is that thermal motion of the ligands has very little effect upon them (as is not the case in the 3d situation), so the f–f absorption bands in the spectra are very narrow, almost as narrow as for free (gaseous) ions.

### 5.3.1 Electronic Spectra

Most lanthanide ions absorb electromagnetic radiation, particularly in the visible region of the spectrum, exciting the ion from its ground state to a higher electronic state, as a consequence of the partly filled 4f subshell. The f–f transitions are excited both by magnetic dipole and electric dipole radiation. Normally the magnetic dipole transitions would not

be seen, but in the case of the lanthanides the electric dipole transitions are much weaker than for transition metal complexes and magnetic dipole transitions can often be seen, especially in fluorescence spectra. The magnetic dipole transitions are parity-allowed, whilst the electric dipole transitions are parity-forbidden ('Laporte-forbidden') in the same sense as d–d transitions in transition metal ions. The f–f transitions gain intensity through mixing in higher electronic states (including d states) of opposite parity, either through the (permanent) effects of a low-symmetry ligand field or through asymmetric molecular vibrations that momentarily destroy any centre of symmetry – 'vibronic coupling' – though the effect is still weaker than in transition metal complexes.

Not all the lanthanide ions give rise to f–f transitions, including obviously the  $f^0$  and  $f^{14}$  species,  $\text{La}^{3+}$  and  $\text{Lu}^{3+}$ . Likewise there are no f–f transitions for the  $f^1$  ( $\text{Ce}^{3+}$ ) and  $f^{13}$  ( $\text{Yb}^{3+}$ ) ions, as with only a single L-value there is no upper 4f state. Transitions between  $^2F_{5/2}$  and  $^2F_{7/2}$  are seen in the case of  $\text{Ce}^{3+}$  as a rather broad band in the infrared region around  $2000\text{ cm}^{-1}$ .  $\text{Ce}^{3+}$  and  $\text{Yb}^{3+}$  do, however, give rise to broad  $4f^n \rightarrow 4f^{n-1}5d^1$  transitions (as indeed do many lanthanides). Even an ion like  $\text{Eu}^{3+}$ , which has several absorptions in the visible region of the spectrum, has only weak absorptions, so many of its compounds appear colourless; the only three tripositive ions whose compounds are invariably coloured are  $\text{Pr}^{3+}$ ,  $\text{Nd}^{3+}$ , and  $\text{Er}^{3+}$ .

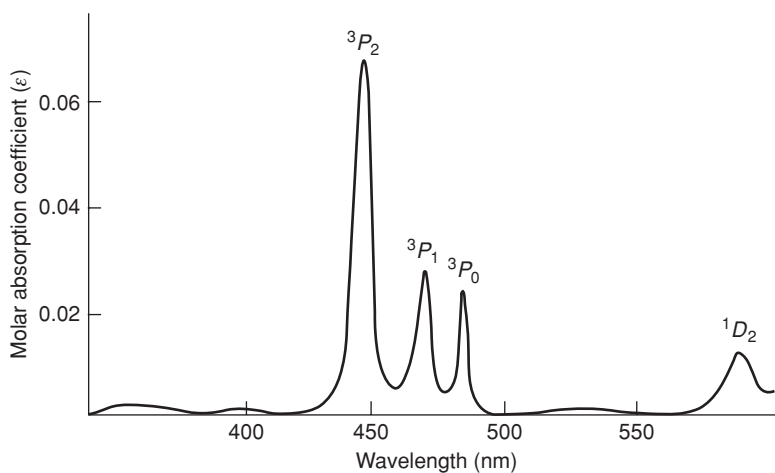
Colours of the  $\text{Ln}^{3+}$  ions in aqueous solution are listed in Table 5.2. A typical spectrum is that of  $\text{Pr}^{3+}$ , shown in Figure 5.4; note the sharp absorption bands, with extinction coefficients below unity.

The electronic spectra of lanthanide compounds resemble those of the free ions, in contrast to the norm in transition metal chemistry; the crystal-field splittings can be treated as a perturbation on the unsplit  $^{2S+1}L_J$  levels. Complexes thus have much the same colour as the corresponding aqua ions. Thus one cannot distinguish between coordination geometries as with octahedrally and tetrahedrally coordinated  $\text{Co}^{2+}$ , for example (let alone note profound colour differences). As already noted, a further consequence of the weak CF splittings is the sharpness of the f–f transitions. The spectrum of the complex  $\text{Eu}(\text{NO}_3)_3(15\text{-crown-5})$  shown in Figure 5.5 is another example of this.

The previous discussion has centred upon the  $\text{Ln}^{3+}$  ions. Most  $\text{Ln}^{2+}$  ions are not stable in solution, but have been prepared artificially in lattices by doping  $\text{CaF}_2$  with the  $\text{Ln}^{3+}$

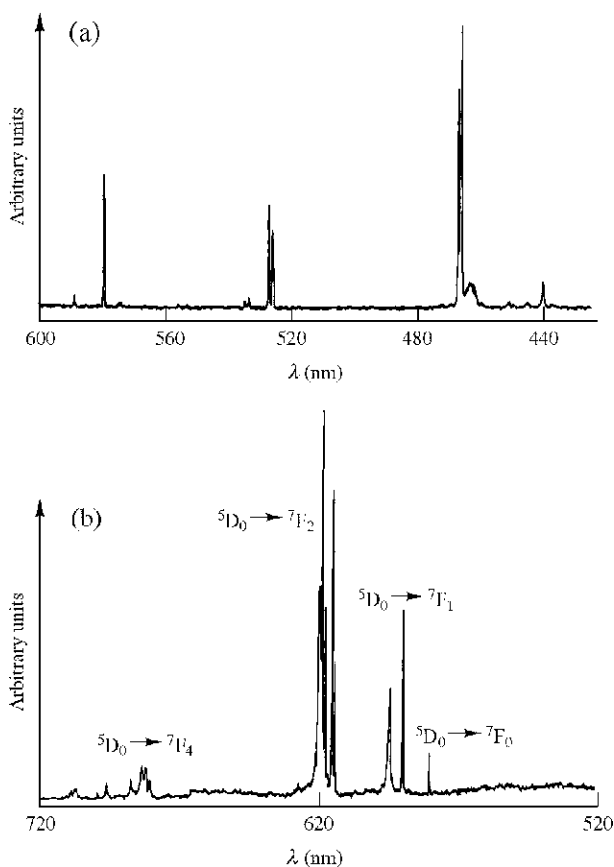
**Table 5.2** Colours of  $\text{Ln}^{3+}$  ions in aqueous solution

	$f^n$	Colour
$\text{La}^{3+}$	$f^0$	Colourless
$\text{Ce}^{3+}$	$f^1$	Colourless
$\text{Pr}^{3+}$	$f^2$	Green
$\text{Nd}^{3+}$	$f^3$	Violet
$\text{Pm}^{3+}$	$f^4$	Pink
$\text{Sm}^{3+}$	$f^5$	Pale yellow
$\text{Eu}^{3+}$	$f^6$	Colourless
$\text{Gd}^{3+}$	$f^7$	Colourless
$\text{Tb}^{3+}$	$f^8$	V.pale pink
$\text{Dy}^{3+}$	$f^9$	Pale yellow
$\text{Ho}^{3+}$	$f^{10}$	Yellow
$\text{Er}^{3+}$	$f^{11}$	Rose
$\text{Tm}^{3+}$	$f^{12}$	Pale green
$\text{Yb}^{3+}$	$f^{13}$	Colourless
$\text{Lu}^{3+}$	$f^{14}$	Colourless



**Figure 5.4**

Electronic absorption bands in the spectrum of  $\text{PrCl}_3$  (aq) reproduced with permission from S.A. Cotton, *Lanthanides and Actinides*, Macmillan (1991) p. 30.



**Figure 5.5**

(a) Excitation spectrum at 77 K of  $\text{Eu}(\text{NO}_3)_3 \cdot 15\text{-crown-5}$  ( $\lambda_{\text{anal}} = 618$  nm). (b) Fluorescence spectrum at 77 K ( $\lambda_{\text{exc}} = 397.7$  nm) (reproduced by permission of the American Chemical Society from J.-C.G. Bunzli, B. Klein, G. Chapuis, and K.J. Schenk, *Inorg. Chem.*, 1982, **21**, 808).

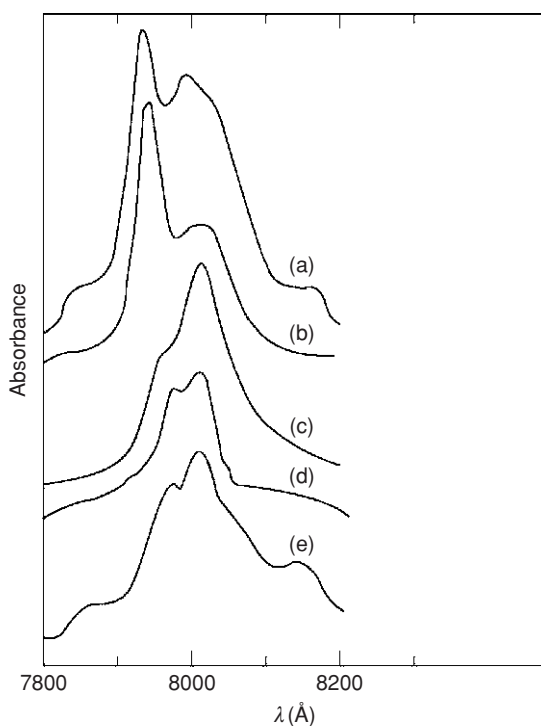
ions, then  $\gamma$ -irradiating. The reduced charge of the  $\text{Ln}^{2+}$  ion causes the energy levels to be closer together, so the ions have different colours; thus whilst  $\text{Gd}^{3+}$  ions are colourless, the isoelectronic ( $f^7$ )  $\text{Eu}^{2+}$  ions are yellow.

### 5.3.2 Hypersensitive Transitions

In contrast to the situation with the 3d transition metals in particular, the 4f–4f transitions in the electronic spectra of lanthanide complexes rarely serve any diagnostic purpose. It may be noted, however, that the spectra of the octahedral  $[\text{LnX}_6]^{3-}$  ions ( $X = \text{Cl}, \text{Br}$ ) have particularly small extinction coefficients, an order of magnitude lower than the corresponding aqua ions, due to the high symmetry of the environment.

Some transitions are ‘hypersensitive’ to changes in the symmetry and strength of the ligand field; as a result, they display shifts of the absorption bands, usually to longer wavelength, as well as band splitting and intensity variation. It is most marked for  $\text{Ho}^{3+}$ ,  $\text{Er}^{3+}$  and particularly for the  $^4\text{I}_{9/2} \rightarrow ^2\text{H}_{9/2}$ ,  $^4\text{F}_{5/2}$  and  $^4\text{I}_{9/2} \rightarrow ^4\text{G}_{5/2}$ ,  $^4\text{G}_{7/2}$  transitions in the case of the  $\text{Nd}^{3+}$  ion.

Figure 5.6 demonstrates how the profile of the band caused by the  $^4\text{I}_{9/2} \rightarrow ^2\text{H}_{9/2}$ ,  $^4\text{F}_{5/2}$  transition in the spectrum of  $\text{Nd}^{3+}$  (aq) resembles that of the tricapped trigonal prismatic



**Figure 5.6**

Spectra of the  $\text{Nd}^{3+} \ ^4\text{I}_{9/2} \rightarrow ^2\text{H}_{9/2}, ^4\text{F}_{5/2}$  transitions: (a) solid  $\text{Nd}(\text{BrO}_3)_3 \cdot 9\text{H}_2\text{O}$ ; (b)  $5.35 \times 10^{-2}\text{M}$   $\text{Nd}^{3+}$  (aq); (c)  $5.35 \times 10^{-2}\text{M}$   $\text{Nd}^{3+}$  in 11.4M HCl; (d) solid  $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$ ; (e) Solid  $\text{Nd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$  (reproduced by permission of the American Chemical Society from D.G. Karraker, *Inorg. Chem.*, 1968, 7, 473).

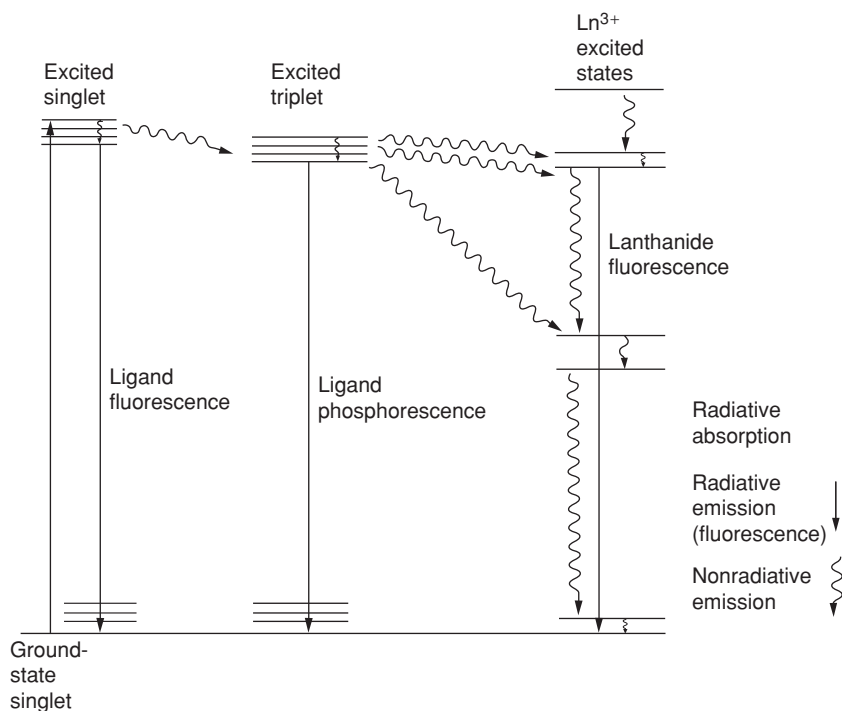
$[\text{Nd}(\text{H}_2\text{O})_9]^{3+}$  ions in  $\text{Nd}(\text{BrO}_3)_3 \cdot 9\text{H}_2\text{O}$ , but is significantly different from that of the 8-coordinate  $\text{Nd}^{3+}$  in the hydrated sulfate and chloride salts. This was important evidence in favour of the aqua ion being 9 coordinate. The spectrum of  $\text{Nd}^{3+}$  in concentrated  $\text{HCl}$  is significantly different, and suggests that an 8-coordinate species is present here.

## 5.4 Luminescence Spectra

Many lanthanide ions exhibit luminescence, emitting radiation from an excited electronic state, the emitted light having sharp lines characteristic of f–f transitions of a  $\text{Ln}^{3+}$  ion. As will be seen later, this can be enhanced considerably by attaching a suitable organic ligand (e.g. a  $\beta$ -diketonate, phenanthroline, crown ether, etc.) to the lanthanide.

The process occurs as summarized in Figure 5.7.

The mechanism of luminescence of a lanthanide complex is as follows. An electron is promoted to an excited singlet state in a ligand upon absorption of a quantum of energy (e.g. from ultraviolet light). This photon drops back to the lowest state of the excited singlet, from where it can return to the ground state directly (ligand fluorescence) or follow a non-radiative path to a triplet state of the ligand. Thence it may either return to the ground state (phosphorescence) or alternatively undergo non-radiative intersystem crossing, this time to a nearby excited state of a  $\text{Ln}^{3+}$  ion, whence it can return to the ground state either by non-radiative emission or by metal-ion fluorescence involving an f–f transition.



**Figure 5.7**  
Luminescence in lanthanide complexes.

Certain  $\text{Ln}^{3+}$  ions have excited states lying slightly lower in energy than the triplet states of typical ligands, and exhibit strong metal-ion fluorescence, most markedly for  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$ , and possibly for others such as  $\text{Sm}^{3+}$  and  $\text{Dy}^{3+}$ . Among the other  $\text{Ln}^{3+}$  ions,  $\text{La}^{3+}$  and  $\text{Lu}^{3+}$  have no  $f^n$  excited state;  $\text{Gd}^{3+}$  has all its excited states above the ligand triplet states while the others have a large number of excited states promoting energy loss by a non-radiative route.  $\text{Tb}^{3+}$  and  $\text{Eu}^{3+}$  are thus the two most useful ions for these studies. They luminesce with green and red colours, respectively. For  $\text{Tb}^{3+}$  the main emissions responsible are  $^5\text{D}_4 \rightarrow ^7\text{F}_n (n = 6-0)$  with  $^5\text{D}_4 \rightarrow ^7\text{F}_5$  the strongest, whilst for  $\text{Eu}^{3+}$ ,  $^5\text{D}_0 \rightarrow ^7\text{F}_n$  are seen ( $n = 4-0$ ) with the transitions to  $^7\text{F}_0$ ,  $^7\text{F}_1$ , and  $^7\text{F}_2$  the most useful. The process is important in lighting applications, and also in both qualitative and quantitative analysis, and in luminescent imaging.

Although the energy level separations are little affected by ligand, nevertheless they are not the same in all complexes. Careful study of the  $^7\text{F}_0 \rightarrow ^5\text{D}_0$  separation in a number of  $\text{Eu}^{3+}$  complexes has shown its shift towards lower energies to depend upon the donor atoms involved, the actual values of the separation varying between  $17\,232\text{ cm}^{-1}$  in  $[\text{Eu}(\text{dpa})_3]^{3-}$  (dpa = dipicolinate) and  $17\,280\text{ cm}^{-1}$  in  $[\text{Eu}(\text{H}_2\text{O})_9]^{3+}$  in some 30 complexes studied, reflecting changes in covalency in the bond.

The ligand field in a complex ion removes the degeneracy of a given  $^{2S+1}L_J$  term partly or completely, the extent of this and the resultant splitting of the emission line depending upon the symmetry of the ligand field (Table 5.3). This means that, in many cases, the individual transitions in the luminescence spectra consist of more than one line (subject to resolution).

Study of the intensity and splitting pattern of certain transitions in the fluorescence spectra of compounds of  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$  in particular can give a good deal of information about the environment of the lanthanide ion. The rules are summarized in Tables 5.4 and 5.5 for both europium and terbium. Owing to the weakness of the electric dipole transitions, the magnetic dipole transitions are of comparable intensity. (For  $\text{Eu}^{3+}$ ,  $^5\text{D}_0 \rightarrow ^7\text{F}_x$  are predominantly electric dipole for  $x$  even, magnetic dipole for  $x$  odd).

**Table 5.3** Number and degeneracy of  $^5\text{D}_0 \rightarrow ^7\text{F}_J$  transitions of  $\text{Eu}^{3+}$  ions in some common symmetries

	$^7\text{F}_0$	$^7\text{F}_1$	$^7\text{F}_2$	$^7\text{F}_3$	$^7\text{F}_4$
Symmetry	ED	MD	ED	ED	ED
$\text{I}_h$	none	$\text{T}_{1g}$	none	none	none
$\text{O}_h$	none	$\text{T}_{1g}$	none	$\text{T}_{1g}$	none
$\text{T}_d$	none	$\text{T}_1$	$\text{T}_2$	$\text{T}_1$	$\text{T}_2$
$\text{D}_{4h}$	none	$\text{A}_{2g} + \text{E}_g$	$\text{E}_g$	$\text{A}_{2g} + \text{E}_g$	none
$\text{D}_{4d}$	none	$\text{A}_2 + \text{E}_3$	$\text{E}_1$	$\text{A}_2 + \text{E}_3$	$\text{B}_2 + \text{E}_1$
$\text{D}_{2d}$	none	$\text{A}_2 + \text{E}$	$\text{B}_2 + \text{E}$	$\text{B}_2 + 2\text{E}$	$\text{B}_2 + 2\text{E}$
$\text{D}_{3h}$	none	$\text{A}'_2 + \text{E}''$	$\text{E}'$	$\text{A}'_2 + \text{E}''$	$\text{A}'_2 + 2\text{E}'$
$\text{D}_{3d}$	none	$\text{A}_{2g} + \text{E}_g$	$\text{A}_{1g} + \text{E}_g$	none	none
$\text{D}_3$	none	$\text{A}_2 + \text{E}$	$2\text{E}$	$2\text{A}_2 + 2\text{E}$	$\text{A}_2 + 3\text{E}$
$\text{C}_{3v}$	$\text{A}_1$	$\text{A}_2 + \text{E}$	$\text{A}_1 + 2\text{E}$	$\text{A}_1 + 2\text{E}$	$2\text{A}_1 + 3\text{E}$
$\text{C}_3$	$\text{A}$	$\text{A} + \text{E}$	$\text{A} + 2\text{E}$	$3\text{A} + 2\text{E}$	$3\text{A} + 3\text{E}$
$\text{C}_{2v}$	$\text{A}_1$	$\text{A}_2 + \text{B}_1 + \text{B}_2$	$2\text{A}_1 + \text{B}_1 + \text{B}_2$	$\text{A}_1 + 2\text{B}_1 + 2\text{B}_2$	$3\text{A}_1 + 2\text{B}_1 + 2\text{B}_2$
$\text{C}_2$	$\text{A}$	$\text{A} + 2\text{B}$	$3\text{A} + 2\text{B}$	$3\text{A} + 4\text{B}$	$5\text{A} + 4\text{B}$
$\text{C}_i$	$\text{A}$	$3\text{A}$	$5\text{A}$	$7\text{A}$	$9\text{A}$
$\text{C}_s$	$\text{A}'$	$\text{A}' + 2\text{A}''$	$3\text{A}' + 2\text{A}''$	$3\text{A}' + 4\text{A}''$	$5\text{A}' + 4\text{A}''$

**Table 5.4** Features of  $^5D_0 \rightarrow ^7F_J$  luminescent transitions for  $\text{Eu}^{3+}$ 

$J$	Main character	Region (nm)	Intensity	Comments
0	ED	577–581	V.weak	Absent in high symmetry – ‘forbidden’
1	MD	585–600	Strong	Intensity largely independent of environment
2	ED	610–625	V.weak to v.strong	Absent if ion on inversion centre; hypersensitive
3	ED	640–655	V.weak	‘Forbidden’
4	ED	680–710	Medium to strong	Environment-sensitive

**Table 5.5** Features of  $^5D_4 \rightarrow ^7F_J$  luminescent transitions for  $\text{Tb}^{3+}$ 

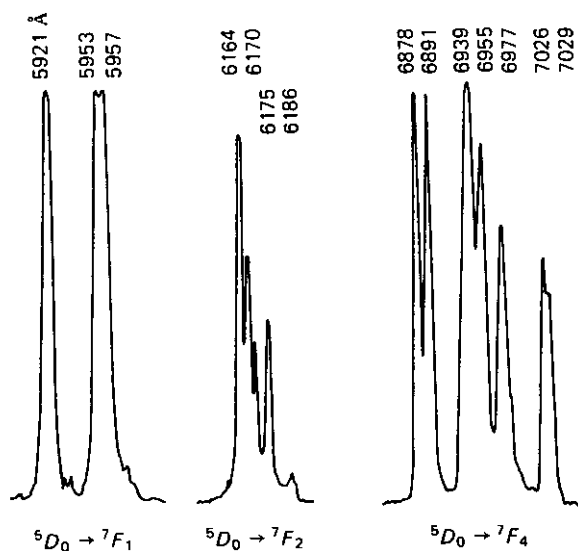
$J$	Region (nm)	Intensity	Comments
6	480–505	Medium to strong	Environment-sensitive
5	535–555	Strong to v.strong	Good probe
4	580–600	Medium to strong	Environment-sensitive
3	615–625	Medium	
2	640–655	Weak	Environment-sensitive

As the luminescence technique is one that can be applied particularly to lanthanide complexes we will discuss it in some depth; and since interpretation is simplest in the case of  $\text{Eu}^{3+}$ , so discussion will centre on that, particularly since it is most involved in applications. In the case of the europium(III) ion, the  $^7F_0$  ground state is unsplit, so that transitions to it give straightforward information about the excited state. Because the  $^5D_0$  state is also unsplit, if more than one component is seen for this transition, it shows more than one europium site. This can be seen in the luminescence spectrum of the crown-ether complex  $[\text{Eu}(\text{NO}_3)_3(15\text{-crown-5})]$  shown in Figure 5.5, which gives some useful information. This compound contains a pentadentate macrocycle and three bidentate nitrates, leading to 11-coordinate europium. A single, very sharp line is seen for the  $^5D_0 \rightarrow ^7F_0$  transition, indicating only one europium site. Secondly, the fact that this electric-dipole transition is seen indicates that the site symmetry is not especially high (i.e. it is not on an inversion centre). The  $^5D_0 \rightarrow ^7F_1$  transition (magnetic-dipole allowed and relatively insensitive to environment) appears as a doublet and singlet, a splitting consistent with the approximately pentagonal pseudosymmetry seen in its crystal structure (in a lower-symmetry environment, the doublet would be further split). The  $^5D_0 \rightarrow ^7F_2$  transition is electric dipole in origin; again, it is absent if the ion is on an inversion centre, and its intensity is very sensitive to environment, making it a good ‘probe’, so its strength here indicates a relatively low symmetry of the site.

An important example historically of the application of luminescence spectroscopy (1969) is  $[\text{Eu}(\text{terpy})_3](\text{ClO}_4)_3$ , whose spectrum (Figure 5.8) supported the assigned geometry before crystallographic details were available (crystallographic structural determination was a *much* slower business at that time). The  $^5D_0 \rightarrow ^7F_0$  transition is absent, whilst the  $^5D_0 \rightarrow ^7F_1$  transition consists of a singlet and a very slightly split (0.4 nm) doublet. The  $^5D_0 \rightarrow ^7F_2$  transition is two split doublets, whilst the  $^5D_0 \rightarrow ^7F_4$  transition is composed of three slightly split doublets and a singlet. If the symmetry were perfectly  $D_3$ , none of the doublets would be split (check Table 5.3), so these splittings can be explained by a very slight descent of symmetry below  $D_3$ .

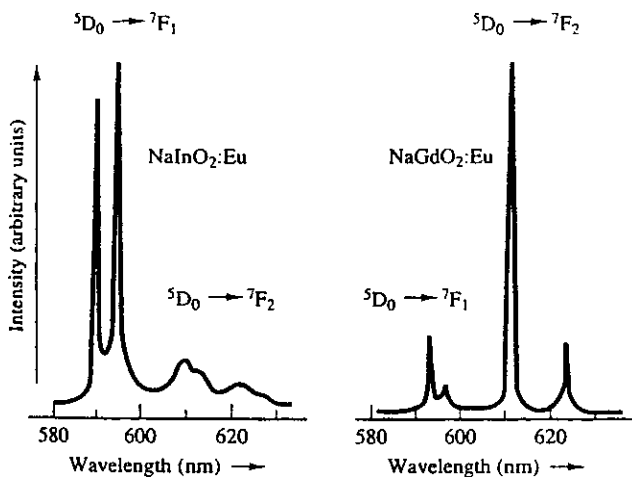
The effect of site symmetry upon luminescence is not confined to structural determination, it also affects lighting applications. Compare the emissions of  $\text{Eu}^{3+}$  in the two oxides  $\text{NaInO}_2$  and  $\text{NaGdO}_2$  (Figure 5.9); both have structures based on  $\text{NaCl}$ , but in



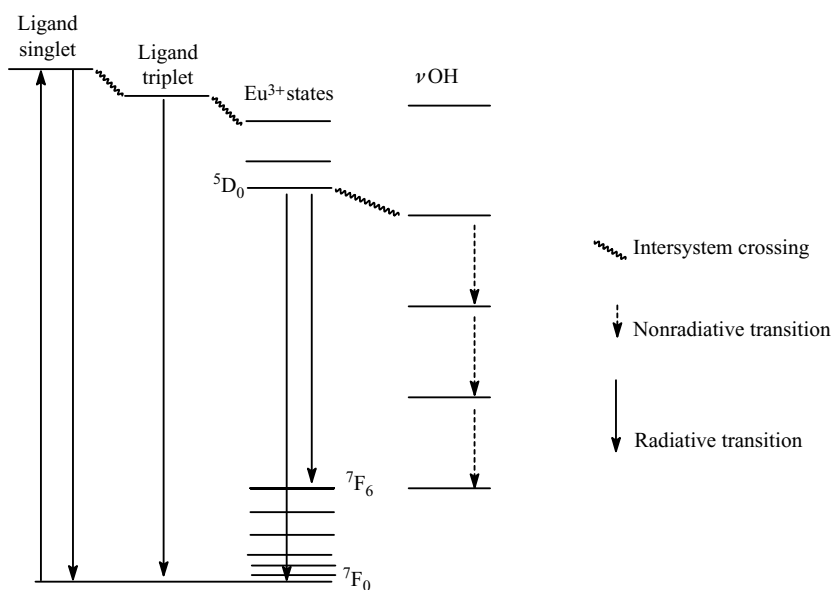
**Figure 5.8**

Fluorescence spectrum of  $[\text{Eu}(\text{terpy})_3]^{3+}$  ions in  $[\text{Eu}(\text{terpy})_3](\text{ClO}_4)_3$ , reproduced from D.A. Durham, G.H. Frost, and F.A. Hart, *J. Inorg. Nucl. Chem.*, 1969, **31**, 833 by permission of Pergamon Press PLC.

the former the europium ions are on centrosymmetric sites, so the  $^5D_0 \rightarrow ^7F_2$  transition is absent, and the emission is predominantly around 590 nm from the  $^5D_0 \rightarrow ^7F_1$  transition. In the case of  $\text{Eu}^{3+}$  in  $\text{NaGdO}_2$ , the europium site lacks an inversion centre, so in this case the emission is largely from the strongly radiating (electric dipole allowed)  $^5D_0 \rightarrow ^7F_2$  transition at 610 nm, the difference in wavelength producing a significant shift in colour (see section 5.4.4 for more on this).

**Figure 5.9**

Luminescence from  $\text{Eu}^{3+}$  substituted in  $\text{NaInO}_2$  and  $\text{NaGdO}_2$ , showing the effect of site symmetry upon emission (adapted from on B. Blasse and A. Bril, *J. Chem. Phys.*, 1966, **45**, 3327).



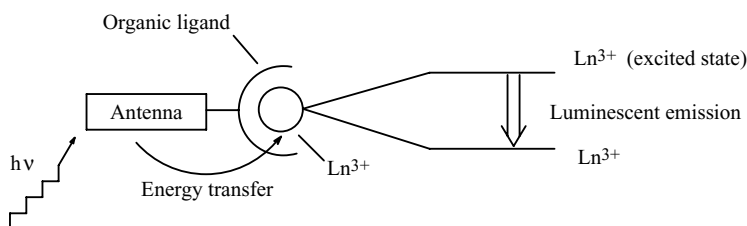
**Figure 5.10**  
Quenching of luminescence of  $\text{Eu}^{3+}$ .

### 5.4.1 Quenching

One problem with luminescence in aqueous solution is that another pathway is available for deactivation of the excited state of the lanthanide, in the form of vibrational energy transfer to water molecules in particular. Figure 5.10 shows this process [in addition to showing the processes involved in  $\text{Eu}^{\text{III}}$  luminescence (only a selection of the radiative transitions are shown)]. This ‘quenching’ of luminescence can be minimized (apart from working in the solid state, or using non-aqueous solvents) by using multidentate ligands which exclude waters from the coordination sphere of the metal, and also by using ligands which tend to encapsulate the lanthanide ion.

### 5.4.2 Antenna Effects

Luminescence from lanthanides is inherently weak (Laporte-forbidden transitions). Deactivation by vibrational transfer can be reduced, as discussed in the last section; another way that gives considerably enhancement is to use a chromophore as a ligand, which absorbs a suitable wavelength of radiation strongly (acts as an ‘antenna’) which it can then transfer to the lanthanide and excite it to the emissive state, using excitation in the region 330–430 nm (Figure 5.11). The most likely acceptor levels for  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$  are 17 200 and 20 400  $\text{cm}^{-1}$  respectively, so the triplet level in the acceptor ligand needs to be above 22 000  $\text{cm}^{-1}$ , otherwise competing thermally activated back-energy-transfer occurs. Some of the most suitable ligands that have been utilized in the past 20 years include Lehn’s tris(bipyridyl) cryptand; calixarenes; and substituted macrocycles containing phenanthridines. The acceptor chromophore does not need to be directly bound to the lanthanide, but should be close for best results. Some lanthanides emit in the near-IR, notably  $\text{Yb}^{3+}$ ,  $\text{Nd}^{3+}$ , and  $\text{Er}^{3+}$ ; these can be excited directly with an optical parametric oscillator.



**Figure 5.11**  
The 'Antenna' effect.

### 5.4.3 Applications of Luminescence to Sensory Probes

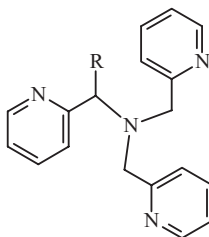
There is considerable interest in using lanthanide complexes as probes for the presence of particular cations and anions, oxygen, etc., with obvious potential in biological, clinical, and environmental applications. Some examples follow.

Luminescence of the  $\text{Eu}^{3+}$  complex of the tetradentate tris(2-pyridylmethyl)amine ligand shown in Figure 5.12 ( $\text{R} = \text{Me}$ ) shows a particular sensitivity for nitrate (over other ions such as chloride, sulfate, and acetate), greatest enhancement of the luminescence spectrum being for the 'hypersensitive'  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  transition at 618 nm, as might be expected (see T. Yamada, S. Shinoda, and H. Tsukube, *Chem. Commun.*, 2002, 218).

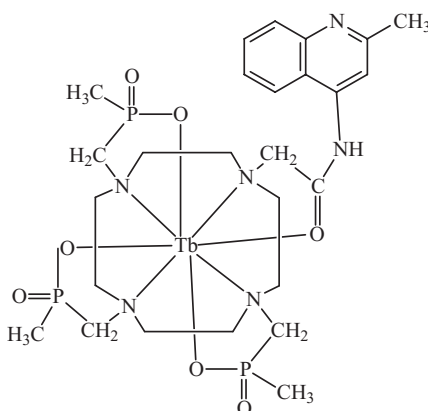
The terbium complex, in contrast, exhibits greatest sensitivity for chloride. Using the achiral ligand ( $\text{R} = \text{H}$ ) exhibits similar selectivity for these anions, but with rather less sensitivity.

A terbium complex (Figure 5.13) is a molecular logic gate corresponding to a two-input INHIBIT function; the output (a terbium emission line) is observed only when the 'inputs', the presence of proteins and the absence of oxygen, are both satisfied.

A similar complex (Figure 5.14,  $\text{M} = \text{Tb}$ ) exhibits a luminescence enhancement by a factor of 125, comparing the emissive neutral complex with its protonated form (pH 3), protonation (of the phenanthridyl nitrogen) suppressing electron transfer. Protonation reduces the energy of the ligand triplet state (the triplet is  $1500\text{ cm}^{-1}$  higher than the terbium  $^5\text{D}_4$  state in the neutral complex, compared with only  $800\text{ cm}^{-1}$  higher in the protonated form), favouring deactivation of the terbium complex by back-energy-transfer to the triplet. Conversely, ligand-based fluorescence increases appreciably on protonation. The triplet state of the phenanthridyl moiety is quenched by  $\text{O}_2$ , so removing oxygen from a solution of the complex steadily increases the terbium lifetime and emission intensity. This complex thus acts as an oxygen sensor, as does the N-methylated analogue (independent of pH in the range 2–9). As strong terbium luminescence only occurs in the absence of both acid and



**Figure 5.12**  
A tris(2-pyridylmethyl)amine ligand.

**Figure 5.13**

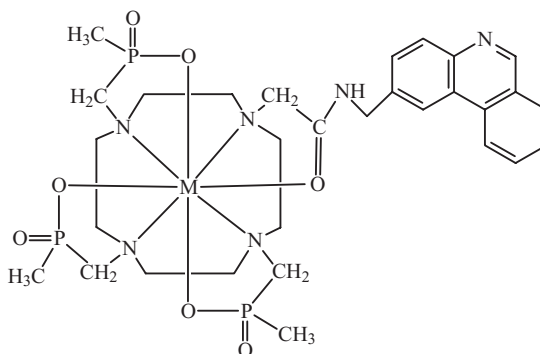
See T. Gunnlaugsson, D.A. MacDonail, and D. Parker, *Chem. Commun.*, 2000, 93.

O<sub>2</sub>, this complex can be considered as a molecular NOR gate, with H<sup>+</sup> and O<sub>2</sub> as inputs and the Tb luminescence as the output.

The europium complex of this ligand (Figure 5.14, M = Eu) exhibits considerable Eu<sup>3+</sup> luminescence enhancement on acidification, comparing the neutral complex with the protonated form at pH 1.5. The N-methylated analogue exhibits europium luminescence that is selectively quenched by chloride ions in the presence of phosphate, citrate, lactate, and bicarbonate, all potentially present in a cellular situation, showing potential as a luminescent sensor in bioassays. Such complexes have further been incorporated into sol-gel thin films and glasses that show good stability to leaching and photodegradation.

#### 5.4.4 Fluorescence and TV

Colour televisions and similar displays are the largest commercial market for lanthanide phosphors, with over 100 million tubes manufactured a year. About 2 g of phosphor is used in each tube. The lanthanide involvement in a traditional colour TV tube works along these

**Figure 5.14**

(see D. Parker and J.A.G. Williams, *Chem. Commun.*, 1998, 245; D. Parker, K. Senanaayake, and J.A.G. Williams, *Chem. Commun.*, 1997, 1777).

lines: There are three electron guns firing electron beams at the screen from subtly different angles (using a 'mask' of some kind) to hit clusters, each comprising three phosphor 'dots', each 'dot' emitting a different primary colour, the 'mask' aligned so the appropriate electron gun fires at its matching phosphor. For many years, the red-emitting phosphor has used a  $\text{Eu}^{3+}$  material, originally  $\text{Eu}^{3+}:\text{YVO}_4$ , more recently  $\text{Eu}^{3+}$  in  $\text{Y}_2\text{O}_2\text{S}$  or  $\text{Eu}^{3+}:\text{Y}_2\text{O}_3$ . These are employed in preference to broad-band emitters like  $\text{Ag}:\text{Zn,CdS}$  as although they are energetically less efficient, these 'narrow-band' lanthanide phosphors are brighter (and also match the eye's colour response better). Green light is obtained from either  $\text{Cu,Al}:\text{Zn,CdS}$  or  $\text{Ce}^{3+}:\text{CaS}$  and  $\text{Eu}^{2+}:\text{SrGa}_2\text{S}_4$  (these are 'broad-band' emitters) or the narrow-line  $\text{Tb}^{3+}:\text{La}_2\text{O}_2\text{S}$ .  $\text{Tm}^{3+}:\text{ZnS}$  has been suggested for the blue phosphor but  $\text{Ag,Al}:\text{ZnS}$  is generally used. Development of materials for alternative flat-screens proceeds apace.

### 5.4.5 Lighting Applications

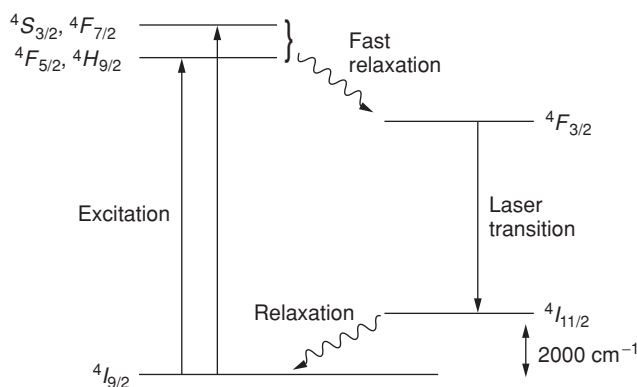
There is intense interest in using rare earths in lighting applications. The so-called tricolour lamps use three narrow-band lanthanide light-emitting materials with maxima around 450, 540, and 610 nm; such as  $\text{Eu}^{2+}:\text{BaMgAl}_{10}\text{O}_{17}$ ;  $(\text{Ce,Gd,Tb})\text{MgB}_5\text{O}_{10}$ ; and  $\text{Eu}:\text{Y}_2\text{O}_3$ , respectively. This gives a good colour rendering at high efficiency. Research continues in developing materials for better projection materials, flat displays, and plasma displays.  $\text{Eu}^{2+}$ -based materials can be used for blue phosphors but tend to suffer from degradation under vacuum UV excitation, whilst a problem with the widely used  $\text{Eu}^{3+}:(\text{Y,Gd})\text{BO}_3$  'red' phosphor is that, owing to the high symmetry of the  $\text{Eu}^{3+}$  site, the  $^5\text{D}_0 \rightarrow ^7\text{F}_1$  emission is very pronounced and the colour is orange-biased (see Section 5.4); however, if the symmetry is too low, there is too much far-red and IR radiation from the  $^5\text{D}_0 \rightarrow ^7\text{F}_{4,6}$  transitions! Thus new materials are continually being synthesized and tested.

One unusual application is a UV emitter containing  $\text{Eu}^{2+}:\text{SrB}_4\text{O}_7$ ; insects can 'see' the UV and be attracted to it, so it has been used in insect traps.

### 5.4.6 Lasers

(Light Amplification by Stimulated Emission of Radiation) Various lanthanide ions can be used in lasers, different ions operating at different frequencies. The most popular, however, is the neodymium laser, most usually using  $\text{Nd}^{3+}$  ions in yttrium aluminium garnet (YAG;  $\text{Y}_3\text{Al}_5\text{O}_{12}$ ). Such a laser functions by increasing light emission by stimulating the release of photons from excited  $\text{Nd}^{3+}$  ions (in this case). A typical device consists of a YAG rod a few cm long (containing about 1% neodymium in place of yttrium) that is fitted with a mirror at each end, one being a partly transmitting mirror (or a similar device). A tungsten-halogen lamp (or some similar device) is used to 'pump' the system to ensure that an excess of  $\text{Nd}^{3+}$  ions is in an excited state (e.g.  $^4\text{F}_{5/2}$  or  $^4\text{F}_{7/2}$ ) so that more ions can emit electrons than can absorb; these excited ions decay rapidly (or 'cascade') to the long-lifetime  $^4\text{F}_{3/2}$  state *non-radiatively*, so that a high proportion of  $\text{Nd}^{3+}$  ions are in this state rather than the ground state, a 'population inversion' (Figure 5.15).

If a photon of the correct energy (at the wavelength of the laser transition) hits a  $\text{Nd}^{3+}$  ion in the  $^4\text{F}_{3/2}$  state, the  $\text{Nd}^{3+}$  ion is stimulated to release another photon of the same wavelength, as it drops to the  $^4\text{I}_{11/2}$  state. As the photons are reflected backwards and forwards in the rod, more and more ions are stimulated into giving up photons (thus depopulating the  $^4\text{F}_{3/2}$  state) and eventually the build up of photons is so great that they emerge from the rod as an intense beam of coherent monochromatic light (wavelength 1.06  $\mu\text{m}$ , in the near-IR). The  $^4\text{I}_{11/2}$  state is an excited level of the ground state, which is not thermally populated and

**Figure 5.15**

A 'four-level'  $\text{Nd}^{3+}$  laser. Reproduced by permission of Macmillan from S.A. Cotton, *Lanthanides and Actinides*, Macmillan, 1991, p. 32.

so undergoes rapid relaxation to the ground state, maintaining the 'population inversion' (whereupon the laser process can recommence). Neodymium is thus said to act as a 'four-level' laser.

### 5.4.7 Euro Banknotes

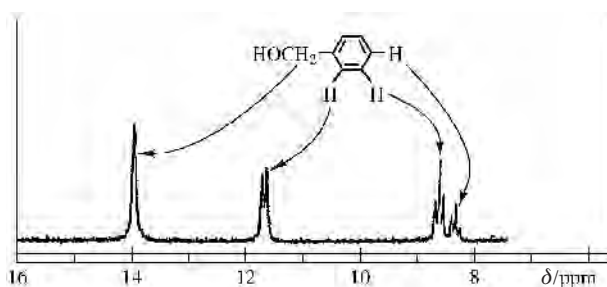
These exhibit green, blue, and red luminescent bands under UV irradiation, as a security measure. The red bands are doubtless due to some  $\text{Eu}^{3+}$  complex, probably with a  $\beta$ -diketonate or some similar ligand. As we have seen, there are  $\text{Eu}^{2+}$  complexes that could cause the green and blue luminescence. Researchers at the University of Twente in the Netherlands suggest that a likely candidate for the source of the green colour is  $\text{SrGa}_2\text{S}_4:\text{Eu}^{2+}$ , and that the blue colour may be caused by  $(\text{BaO})_x \cdot 6\text{Al}_2\text{O}_3:\text{Eu}^{3+}$ . It's quite appropriate that Euro notes contain europium, really.

## 5.5 NMR Applications

### 5.5.1 $\beta$ -Diketonates as NMR Shift Reagents

Paramagnetic lanthanide  $\beta$ -diketonate complexes  $\text{Ln}(\text{R}^1\text{COCHCOR}^2)_3$  produce shifts in the NMR spectra of Lewis base molecules capable of forming adducts with them and are thus often referred to as Lanthanide Shift Reagents (LSRs) though all paramagnetic lanthanide complexes can exhibit shifted resonances. Molecules were chosen, such as  $\text{Eu}(\text{dpm})_3$  ( $\text{R}^1 = \text{R}^2 = \text{Me}_3\text{C}$ ), which were quite soluble in non-polar solvents. The magnitude of the proton shifts depends upon the distance of the proton from the site of coordination to the lanthanide ion.

Immense activity in this area in the early 1970s resulted as the use of LSRs enabled simplification of the spectra of organic molecules without the use of high-frequency spectrometers. The spreading-out of the spectrum and differential nature of the shifts removed degeneracies and overlaps, whilst study of the shifts, particularly when more than one LSR was used, permitted spatial assignment of the protons (or other resonant nucleus) with concomitant structural information about the organic molecule.

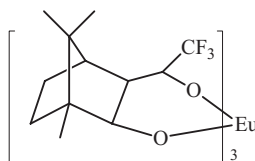


**Figure 5.16**

The 100 MHz proton NMR spectrum of benzyl alcohol in the presence of  $\text{Eu}(\text{dpm})_3$  (0.39 mol) (reproduced by permission of the Royal Society of Chemistry from J.K. M. Sanders and D.H. Williams, *Chem. Commun.*, 1970, 422).

One example of such an application is shown in Figure 5.16. At 100 MHz, the aromatic region of the  $^1\text{H}$  NMR spectrum of  $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$  is a singlet, but on adding  $\text{Eu}(\text{dpm})_3$ , which coordinated to the OH group, the aromatic protons are shifted by amounts that depend on their distance from the Eu and are susceptible to first-order analysis.

Nowadays this technique is less generally used owing to the spread of high-frequency spectrometers, but chiral reagents like a lanthanide camphorato complex find applications [Figure 5.17 shows  $\text{Eu}(\text{tfc})_3$ ], for example, when such a chiral shift reagent binds to a racemic mixture, two diastereoisomeric forms of the complex are formed, each with different peaks in the NMR spectrum; each signal can be integrated and used to calculate the enantiomeric excess, a quick way of estimating the yield of each isomer.



**Figure 5.17**

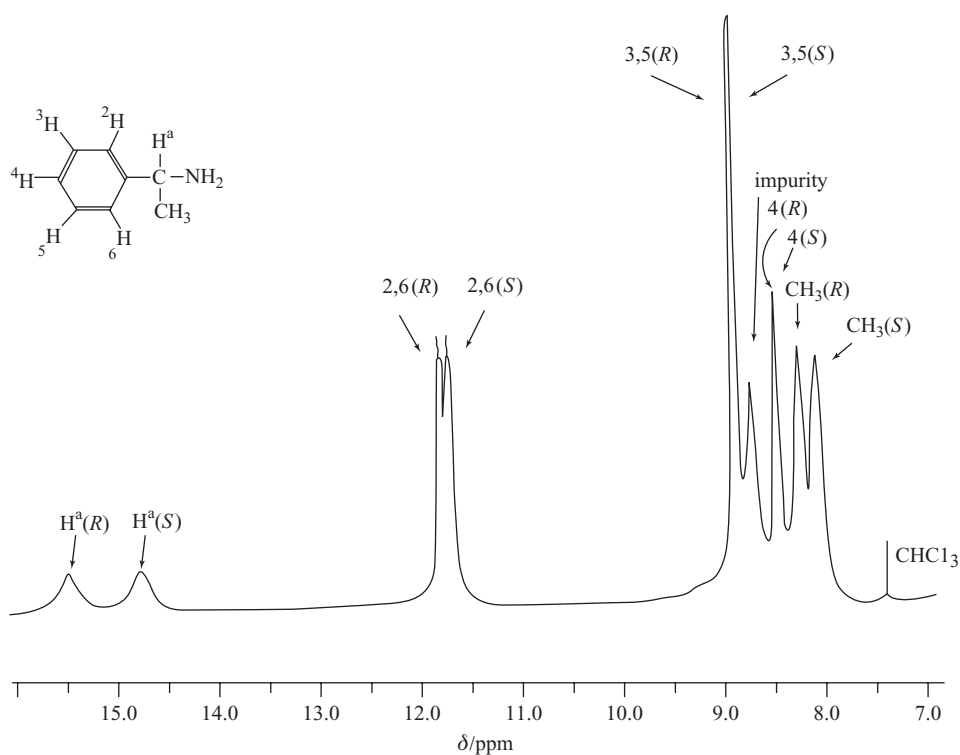
A chiral shift reagent.

Figure 5.18 shows the  $^1\text{H}$  NMR spectrum of a mixture of 1-phenylethylamine and  $\text{Yb}(\text{tfc})_3$  in  $\text{CDCl}_3$ . The (*S*)-(+)- and (*R*)-(–) isomers here give clearly distinguished peaks (the amine resonances are well downfield and not displayed).

### 5.5.2 Magnetic Resonance Imaging (MRI)

The use of gadolinium(III) complexes to assist diagnosis in this expanding area of medicine is now most important.

In the MRI experiment, a human body is placed on a horizontal table that is slid into the centre of the magnetic field of the MRI scanner (essentially a pulsed FT NMR spectrometer). MRI relies on detecting the NMR signals from hydrogen atoms in water molecules (which make up ~60% of the human body) and distinguishes between water molecules in healthy and diseased tissue (since water molecules in cancerous tissue have much longer relaxation times). MRI works well in soft tissue and has been used particularly to identify lesions in the brain and spinal cord. When brain activity occurs, blood flow to that region increases, which causes a contrast change between the active and inactive regions.

**Figure 5.18**

The  $^1\text{H}$  NMR spectrum of a mixture of 1-phenylethylamine and  $\text{Yb}(\text{TFC})_3$  in  $\text{CDCl}_3$  (reproduced with permission of the Editor from T. Viswanathan and A. Toland, *J. Chem. Educ.*, 1995, **72**, 945).

In order to make diagnoses about different parts of the body, it is necessary to obtain a two-dimensional image of the signals. This is done by placing the patient in a magnetic field gradient (using gradient coils to create different fields at many points in a piece of tissue) so that otherwise identical water molecules yield resonances as slightly different frequencies at each point, depending upon their position in the field, with a computer processing the data to give a digitized image of a spatially organized signal. The signal intensity depends upon the relaxation times of the protons, so, in order to enhance the contrast to differentiate between healthy and diseased tissue, paramagnetic contrast agents are used.

### 5.5.3 What Makes a Good MRI Agent?

The choice is dictated by a combination of several factors:

1. High magnetic moment;
2. Long electron-spin relaxation time;
3. Osmolarity similar to serum;
4. Low toxicity;
5. High solubility in water;
6. Targeting tissue;
7. Coordinated water molecules;
8. Large molecule with long rotational correlation times.



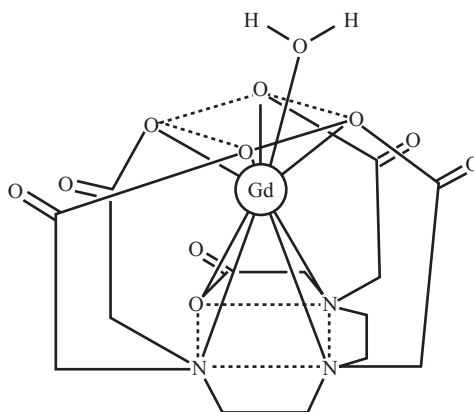
Gadolinium(III) compounds are especially suited to this. The  $\text{Gd}^{3+}$  ion has a large number of unpaired electrons ( $S = 7/2$ ) and moreover its magnetic properties are isotropic. It has a relatively long electron-spin relaxation time,  $\sim 10^{-9}$  s, which makes it more suitable than other very paramagnetic ions such as  $\text{Dy}^{3+}$ ,  $\text{Eu}^{3+}$ , and  $\text{Yb}^{3+}$  ( $\sim 10^{-13}$  s). These factors are very favourable for nuclear spin relaxation.

The free  $\text{Gd}^{3+}(\text{aq})$  ion is toxic, however, with an  $\text{LD}_{50} \sim 0.1$  mmol/kg, less than the imaging dose (normally of the order of 5 g for a human); gadolinium complexes are therefore used, using ligands that form a very stable *in vivo* complex. Another factor is the presence of water molecules in the coordination sphere of gadolinium, as relaxation times are shorter the nearer the water molecules are to the  $\text{Gd}^{3+}$  ion. Ideally the more water molecules present the better, since more solvent waters can readily be exchanged with coordinated water molecules. There is a balance to be struck here, as the use of multidentate ligands to ensure a high stability constant for the gadolinium complex, to minimize the amount of toxic, free  $\text{Gd}^{3+}$  ions present, tends to reduce the number of bound waters, and in practice most contrast agents have one coordinated water molecule.

An obvious early choice for consideration as a MRI agent was the EDTA complex,  $[\text{Gd}(\text{edta})(\text{H}_2\text{O})_3]^-$ . This seemed to combine several highly desirable factors, as it was stable ( $\log K = 17.35$ ); possessed three coordinated water molecules; and utilized a cheap ligand. However, it was found to be poorly tolerated in animal tests (and it was subsequently found that it released significant amounts of free  $\text{Gd}^{3+}$ , despite its high stability constant), so the focus shifted elsewhere. The complex of the octadentate  $\text{DTPA}^{5-}$ ,  $[\text{Gd}(\text{dtpa})(\text{H}_2\text{O})]^{2-}$  (gadopentetate dimeglumine; Magnevist®; Figure 5.19) was an obvious extension ( $\log K \sim 22.5$ ), and this has proved a highly successful compound, the first compound to be approved for clinical applications (1988).

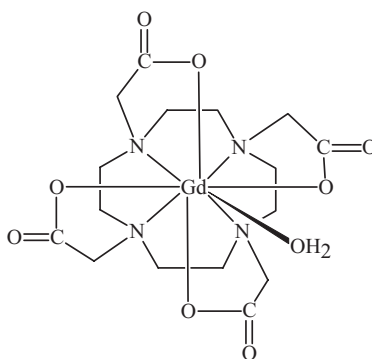
Another compound to be widely used is  $[\text{Gd}(\text{dota})(\text{H}_2\text{O})]^-$  (gadoterate meglumine; Dotarem®; Figure 5.20), using a cyclic ligand in an attempt to form more stable complexes ( $\log K \sim 24\text{--}25$ ). Another example is  $[\text{Gd}(\text{do3a})(\text{H}_2\text{O})_2]$  (Figure 5.21).

Apart from charged species, neutral complexes are also used. One example of this is  $[\text{Gd}\text{-hp}\text{-do3a}]$ ; another is  $[\text{Gd}(\text{dtpa}\text{-bma})(\text{H}_2\text{O})]$  (gadodiamide; Omniscan®; Figure 5.22). In these complexes, the loss of charge is achieved by removing a carboxylate group, or by

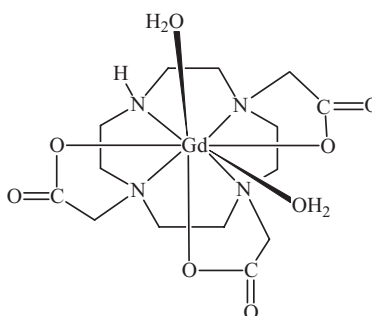


**Figure 5.19**

The structure of  $\text{Gd}(\text{dtpa})(\text{H}_2\text{O})^{2-}$  (reproduced by permission of Macmillan from S.A. Cotton, *Lanthanides and Actinides*, 1991, p. 64).



**Figure 5.20**  
[Gd(dota)(H<sub>2</sub>O)]<sup>-</sup>.



**Figure 5.21**  
[Gd(do3a)(H<sub>2</sub>O)<sub>2</sub>].

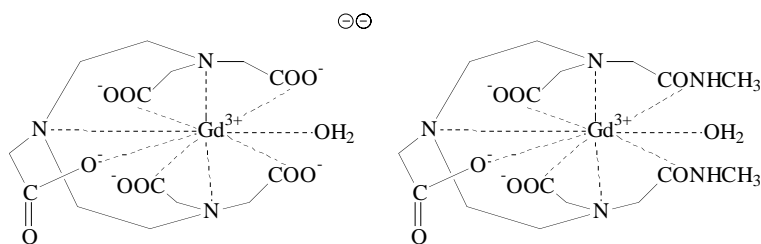
converting two carboxylates into amides, respectively. Both charged and neutral complexes have advantages. Neutral complexes have less osmotic effect, so are more likely to have osmolalities similar to blood, whilst charged species are more hydrophilic, and therefore are more soluble.

Replacement of an NH group in [Gd-(do3a)(H<sub>2</sub>O)<sub>2</sub>] by sidechains containing OH groups was designed to enhance solubility in the agents Gd-hp-do3a (ProHance<sup>®</sup>; Figure 5.23) and Gd-do3a-butrol (Gadovist<sup>®</sup>; Figure 5.24).

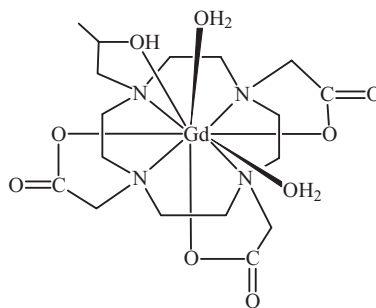
Another gadolinium MRI agent, of a different type, is Gadolite<sup>®</sup> (approved for use in the USA and UK in 1996). This is Gd<sup>3+</sup>-exchanged zeolite NaY that has been shown to be an effective contrast agent for the gastrointestinal tract, defining it from adjacent tissues. With standard MRI imaging techniques, bowel fluid in the gastrointestinal tract can mimic diseases such as tumours. Gadolite is stable at pH 2.5–5 for several hours, and although gadolinium gets leached at lower pH, the oral toxicity of gadolinium is low.

### 5.5.4 Texaphyrins

A new type of complex with a different spectroscopic application is provided by the texaphyrins, compounds of 'extended' porphyrins where the ring contains five donor nitrogens. These have attracted considerable interest because of their possible medicinal applications.



**Figure 5.22**  
(a)  $[\text{Gd}(\text{dtpa})(\text{H}_2\text{O})]^{2-}$ , (b)  $[\text{Gd}(\text{dtpa-bma})(\text{H}_2\text{O})]$ .



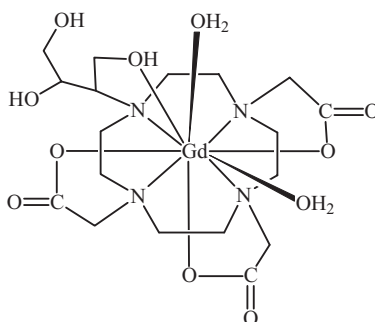
**Figure 5.23**  
 $[\text{Gd}(\text{hp-do3a})(\text{H}_2\text{O})]$ .

Two texaphyrin complexes are undergoing clinical trials; a gadolinium compound (Gd-tex; XCYTRIN<sup>®</sup>; Figure 5.25) is an effective radiation sensitizer for tumour cells. It assists the production of reactive oxygen-containing species, whilst the presence of the  $\text{Gd}^{3+}$  ion means that the cancerous lesions to which it localizes can be studied by MRI. It is being investigated in connection with pancreatic tumours and brain cancers. One form of the lutetium analogue (LUTRIN<sup>®</sup>) is being developed for photodynamic therapy for breast cancer, and another (ANTRIN<sup>®</sup>) is being developed for photoangioplasty, where it has potential for treating arteriosclerosis by removal of atherosclerotic plaque.

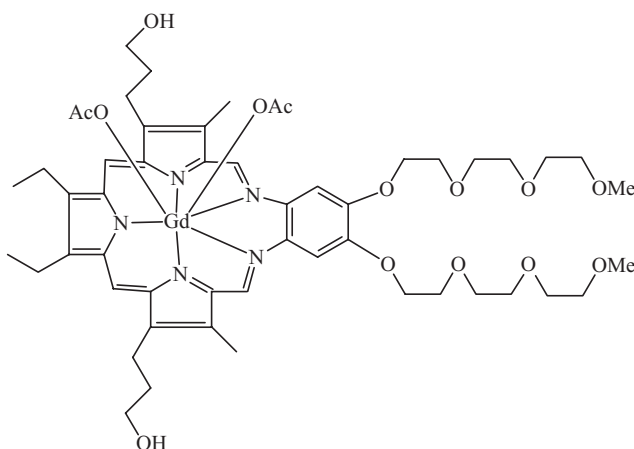
## 5.6 Electron Paramagnetic Resonance Spectroscopy

Although most lanthanide ions are paramagnetic, because of rapid relaxation effects, spectra can be obtained only at low temperatures (often 4.2 K) in most cases. From the point of view of the chemist, EPR spectra are readily obtained (at room temperature) only from the  $f^7 \text{Gd}^{3+}$ , with its  $^8S_{7/2}$  ground state. The sublevels of this state are degenerate in the absence of a crystal field (in a free  $\text{Gd}^{3+}$  ion), but are split into four Kramers' doublets, with  $M_J$ -values of  $\pm 1/2$ ,  $\pm 3/2$ ,  $\pm 5/2$  and  $\pm 7/2$ . The application of a magnetic field removes the degeneracy of each doublet, and transitions can occur on irradiation with microwave radiation, subject to the usual selection rule of  $\Delta M_J = \pm 1$ .

In the absence of a zero-field splitting (z.f.s.), all transitions occur at the same field (corresponding to a  $g$ -value of 2.00), but as the z.f.s. increases, transitions occur at higher



**Figure 5.24**  
[Gd(do3a-butrol)(H<sub>2</sub>O)].

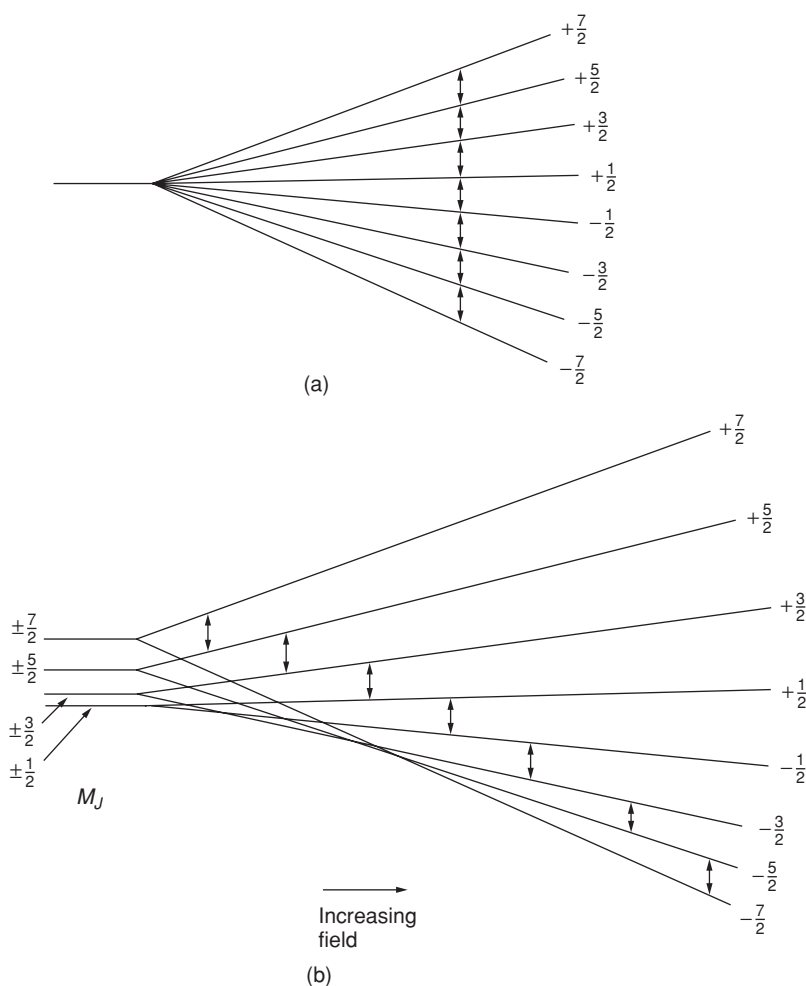


**Figure 5.25**  
Gd-tex.

and lower fields (corresponding to ‘effective’  $g$ -values above and below 2) (Figure 5.26). The situation is not dissimilar to the high-spin  $\text{Cr}^{3+}(\text{d}^3)$  and  $\text{Fe}^{3+}$  and  $\text{Mn}^{2+}(\text{d}^5)$  ions. In the case of the three-coordinate silylamide  $[\text{Ln}[\text{N}(\text{SiMe}_3)_2]_3]$ , where there is a very strong axial distortion, signals are observed with the effective  $g$ -values  $g_{\perp} = 8$ ,  $g_{\parallel} = 2$ .

## 5.7 Lanthanides as Probes in Biological Systems

The lanthanides form a series of ions of closely related size and bonding characteristics and in many respects resemble  $\text{Ca}^{2+}$ , for which they often substitute isomorphously in biological systems. Since different  $\text{Ln}^{3+}$  ions can be probed with particular spectroscopic techniques (e.g.  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$ , fluorescence;  $\text{Gd}^{3+}$ , ESR;  $\text{Nd}^{3+}$ , electronic spectra), in favourable circumstances it should be possible to obtain information about the binding site of spectroscopically inactive  $\text{Ca}^{2+}$  in several ways. Systems studied include the calcium-binding sites in calmodulin, trypsin, parvalbumin, and the Satellite tobacco necrosis virus.

**Figure 5.26**

Showing the effect of zero-field splitting on the EPR transitions in  $\text{Gd}^{3+}$ .

Lanthanide chelates have been used as labels of antigens and antibodies in fluoroimmuno-logical analysis, and in areas such as the determination of steroids in animals, of hormones and viral antigens in humans, and of herbicides in water.

**Question 5.1** Work out the ground states for  $\text{Pm}^{3+}$  ( $f^4$ ),  $\text{Eu}^{3+}$  ( $f^6$ ),  $\text{Er}^{3+}$  ( $f^{11}$ ),  $\text{Pr}^{4+}$  ( $f^1$ ) and  $\text{Eu}^{2+}$  ( $f^7$ ).

**Answer 5.1**  $\text{Pm}^{3+}$  ( $^5\text{I}_4$ );  $\text{Eu}^{3+}$  ( $^7\text{F}_0$ );  $\text{Er}^{3+}$  ( $^4\text{I}_{15/2}$ );  $\text{Pr}^{4+}$  ( $^2\text{F}_{5/2}$ );  $\text{Eu}^{2+}$  ( $^8\text{S}_{7/2}$ ).

**Question 5.2** Calculate the magnetic moment for  $\text{Pr}^{3+}$  ions and  $\text{Dy}^{3+}$  ions.

**Question 5.3** Explain why f–f transitions in the electronic spectra of lanthanide complexes are weaker than d–d transitions in the corresponding spectra of transition metal complexes.

**Answer** Forming a  $\text{Ln}^{3+}$  ion from a lanthanide atom by removing electrons stabilizes the orbitals in the order  $4f > 5d > 6s$ . The  $6s$  and  $5d$  orbitals are emptied and the ions have the electron configurations  $[\text{Xe}] 4f^n$ . The  $4f$  orbitals have become core-like, not involved in bonding, with negligible crystal-field effects. Both  $d-d$  and  $f-f$  transitions are parity-forbidden. In the case of  $d-d$  spectra, vibronic coupling lowers the symmetry round the metal ion, so  $d/p$  mixing can occur and the  $d-d$  transitions are to some extent ‘allowed’. Because the  $4f$  orbitals are so contracted compared with  $d$  orbitals,  $f/p$  mixing and vibronic coupling are much more limited, thus the  $f-f$  transitions are less ‘allowed’ and so extinction coefficients of the absorption bands are smaller.

**Question 5.4** Why is the  $\text{Ce}^{3+}(4f^1)$  ion colourless whereas  $\text{Ti}^{3+}$  solutions ( $3d^1$ ) are purple?

**Question 5.5** Explain why the electronic spectra of  $\text{Pr}^{3+}(4f^2)$  consist of a number of weak sharp lines, whereas those in the spectrum of  $\text{V}^{3+}(3d^2)$  are stronger and broader and less numerous.

**Question 5.6** Why do  $\text{La}^{3+}$ ,  $\text{Lu}^{3+}$ , or  $\text{Gd}^{3+}$  compounds not show luminescence properties?

**Question 5.7** Comment on the emission spectrum of  $[\text{Eu}(\text{Me}_3\text{CCOCHCOCMe}_3)_3(2,9\text{-dimethyl-1,10-phenanthroline})]$  at 77 K (Figure 5.27). It shows the  $^5\text{D}_0 \rightarrow \text{F}^7(J = 0-2)$  transitions. Consult Section 5.4 if required.

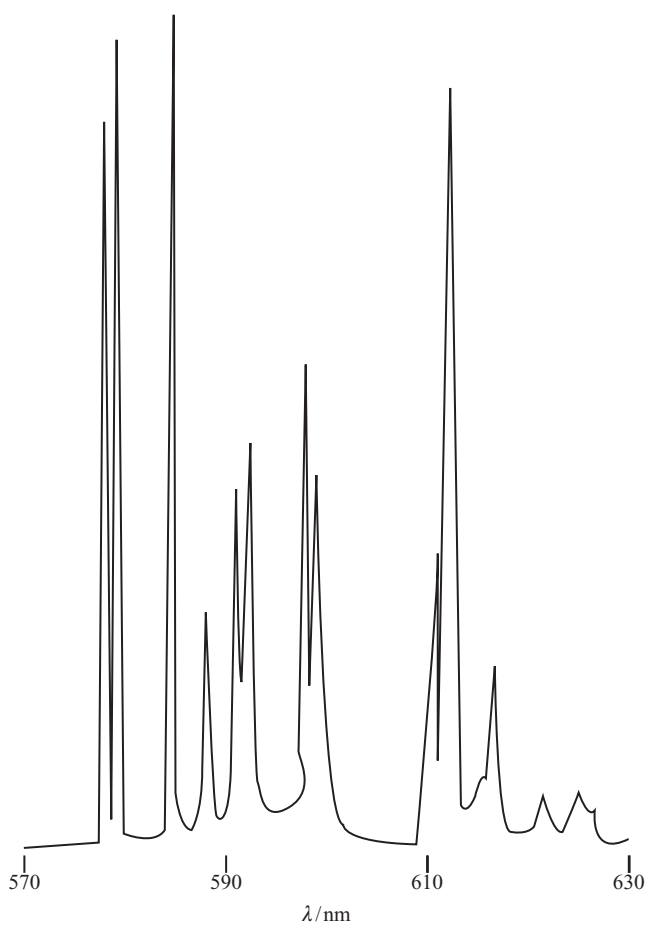
**Comment:** The  $^5\text{D}_0 \rightarrow ^7\text{F}_0$  transition consists of 2 lines (the spacing is 1.17 nm,  $35 \text{ cm}^{-1}$ ), suggesting that there are two different  $\text{Eu}^{3+}$  sites. There are 6 bands in the region of the  $^5\text{D}_0 \rightarrow ^7\text{F}_1$  transition between 584.6 and 598.8 nm, and at least 7 bands in the region of the  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  transition between 610.0 and 616.6 nm.

Consulting Table 5.13 indicates that a maximum of 3 bands is predicted for the former and 5 bands for the latter, again suggesting that there are two distinctly different europium sites. In fact, the crystal structure of this compound shows that there are two distinctly different molecules present in the unit cell, both with square antiprismatic coordination of europium, with occupancy factors of 59% and 41% (see R.C. Holz and L.C. Thompson, *Inorg. Chem.*, 1993, **32**, 5251; another example of this behaviour can be found in D.F. Moser, L.C. Thompson, and V.G. Young, *J. Alloys Compd.*, 2000, **303–304**, 121.)

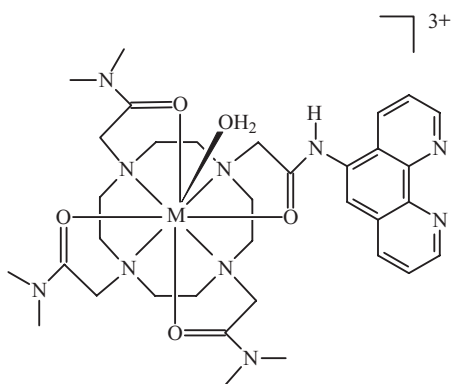
**Question 5.8** The emission of the macrocyclic complex shown in Figure 5.28 ( $\text{M} = \text{Eu}$ ) has been studied as a function of pH and metal ion concentration.

- A.** Emission was weak over the pH range 12–8.5, but on reducing the pH below 8.5 emission was greatly enhanced until it was almost constant between pH 6.5 and 5. On further reduction to pH 3, emission was gradually quenched. These changes were completely reversible. Comment upon this.
- B.** The effect of adding different metals ions on the emission was investigated at pH 7.4. Groups I and II ions, as well as  $\text{Zn}^{2+}$ , had no effect. Addition of  $\text{Cu}^{2+}$  ions shifted the absorption spectrum of the phenanthroline ligand slightly from 255 to 280 nm and caused a substantial quenching of the europium luminescence. This was reversed, with recovery of the europium emission, on adding EDTA solution. Comment on this.

**Answer A.** Excitation of the phenanthroline ‘antennas’ sensitizes the  $\text{Eu}^{3+}$  excited state. Under alkaline conditions, this does not emit, possibly because of reduction to the

**Figure 5.27**

The emission spectrum of  $[\text{Eu}(\text{Me}_3\text{CCOCHCOCMe}_3)_3(2,9\text{-dimethyl-1,10-phenanthroline})]$  at 77 K, showing the  $^5\text{D}_0 \rightarrow \text{F}_J$  ( $J = 0-2$ ) transitions (reproduced with permission of the American Chemical Society from R.C. Holz and L.C. Thompson, *Inorg. Chem.*, 1993, **32**, 5251).

**Figure 5.28**

non-emitting  $\text{Eu}^{2+}$  state or because deprotonation of the amide group affects its ability to populate the excited state of  $\text{Eu}^{3+}$ . In acidic solution, basic nitrogen atoms in the phenanthroline group can be protonated, altering the electronic structure of the ligand and thereby affecting the ability of the ligand to populate the  $^5\text{D}_0$  state of europium.

**Answer B.**  $\text{Cu}^{2+}$  ions have a strong affinity for N-donor ligands like ammonia, so are expected to bind well to phenanthroline (causing the shift in its absorption spectrum). The phenanthroline group acts as an antenna and coordination to copper obviously affects this. EDTA, however, is a hexadentate ligand that binds copper ions more strongly, detaching the copper from the phenanthroline group and restoring its antenna ability.

**Refs:** T. Gunnlaugsson, J.P. Leonard, K. Sénéchal, and A.J. Harte, *J. Am. Chem. Soc.*, 2003, **125**, 12062; T. Gunnlaugsson, J.P. Leonard, K. Sénéchal, and A.J. Harte, *Chem. Commun.*, 2004, 782.

**Question 5.9** List and explain the desirable qualities of a good MRI contrast agent.

**Question 5.10** From your knowledge of the chemistries of calcium and the lanthanides, suggest reasons why lanthanides are good at substituting at calcium-binding sites in, e.g., proteins.

**Answer 5.10** They have similar ionic radii; similar high coordination numbers; both are 'hard' Lewis acids that prefer O-donor ligands.





# 6 Organometallic Chemistry of the Lanthanides

By the end of this chapter you should be able to:

- recall that these compounds are very air- and water-sensitive;
- recall that the bonding has a significant polar character;
- recall that some of these compounds have small molecular structures with appropriate volatility and solubility properties;
- recall appropriate bonding modes for the organic groups;
- recall that these compounds may exhibit low coordination number;
- suggest suitable synthetic routes;
- suggest structures for suitable examples;
- recall that these compounds may be useful synthons (starting materials for synthesis);
- recall that the 18-electron rule is not a predictive tool here.

## 6.1 Introduction

Compounds of these metals involving either  $\sigma$ - or  $\pi$ -bonds to carbon are generally much more reactive to both air and water than those of the d-block metals. Thus there is no lanthanide equivalent of ferrocene, an unreactive air- and heat-stable compound. They are often thermally stable to 100 °C or more, but are usually decomposed immediately by air (and are not infrequently pyrophoric). Within these limitations, lanthanide organometallic compounds have their own special features, often linked with the large size of these metals.

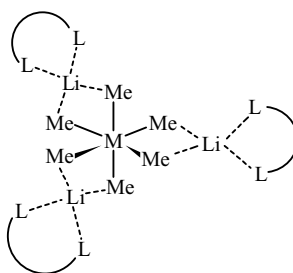
## 6.2 The +3 Oxidation State

As usual with lanthanides, this is the most important oxidation state, but there are compounds in the 0, +2 and +4 oxidation states that are discussed later.

Simple homoleptic  $\sigma$ -bonded alkyls and aryls have been difficult to characterize. They are most readily achieved by using bulky ligands or completing the coordination sphere with neutral ligands or by forming 'ate' complexes.

### 6.2.1 Alkyls

Reaction of 3 moles of methyl lithium with  $\text{LnCl}_3$  ( $\text{Ln} = \text{Y, La}$ ) in THF yielded what are probably  $\text{Ln}(\text{CH}_3)_3$  contaminated with  $\text{LiCl}$  and whose IR spectra showed the presence of

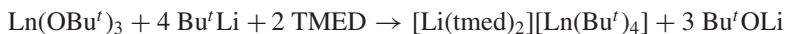
**Figure 6.1**

The structure of  $[\text{Li}(\text{L-L})]_3 [\text{M}(\text{CH}_3)_6]$ .

THF. If an excess of  $\text{CH}_3\text{Li}$  is added to  $\text{MCl}_3$  in THF, in the presence of a chelating ligand ( $\text{L-L}$ ), either tetramethylethylenediamine (tmed or tmeda) or 1,2-dimethoxyethane (dme) complexes  $[\text{Li}(\text{tmed})]_3 [\text{M}(\text{CH}_3)_6]$  or  $[\text{Li}(\text{dme})]_3 [\text{M}(\text{CH}_3)_6]$  are obtained for Sc, Y, and all lanthanides except Eu (see Figure 6.1).

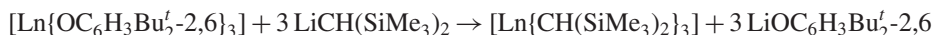


A number of anionic complexes with the bulky *tert*-butyl ligand have been made, containing tetrahedral  $[\text{LnBu}_4']^-$  ions  $\{\text{Ln} = \text{Er, Tb, Lu, confirmed (X-ray) for } [\text{Li}(\text{tmed})_2]^+ [\text{LuBu}_4']^-\}$ .



Moving to the  $\text{CH}_2\text{SiMe}_3$  ligand, the neutral alkyl  $[\text{Sm}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_3]$  has been synthesized and shown to have a *fac*-octahedral structure, whilst  $[\text{Ln}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2]$  ( $\text{Ln} = \text{Er, Yb, Lu}$ ) are five coordinate. It seems that these alkyls are extremely unstable for lanthanides larger than Sm. Anionic species are obtained by reaction with excess of  $\text{LiCH}_2\text{SiMe}_3$  in the presence of THF or TMED to solvate the lithium ion; compounds  $[\text{Li}(\text{thf})_4][\text{Ln}(\text{CH}_2\text{SiMe}_3)_4]$  ( $\text{Ln} = \text{Y, Er, Tb, Yb}$ ) and  $[\text{Li}(\text{tmed})_2][\text{Ln}(\text{CH}_2\text{SiMe}_3)_4]$  ( $\text{Ln} = \text{Y, Er, Yb, Lu}$ ).

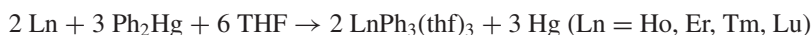
In order to make simple alkyls of the even bulkier  $-\text{CH}(\text{SiMe}_3)_2$  ligand, an indirect approach is needed. Direct reaction of  $\text{LnCl}_3$  with  $\text{LiCH}(\text{SiMe}_3)_2$  in ether solvents gives products like  $[(\text{Et}_2\text{O})_3\text{Li}(\mu\text{-Cl})\text{Y}\{\text{CH}(\text{SiMe}_3)_2\}_3]$ ; this can be avoided by using a chloride-free starting material, by using a solvent like pentane that does not coordinate to an alkali metal, and by using a bulky aryloxide ligand that does not bridge between a lanthanide and lithium. Thus, starting with  $[\text{Ln}\{\text{OC}_6\text{H}_3\text{Bu}'_{2,6}\}_3]$ , alkyls  $[\text{Ln}\{\text{CH}(\text{SiMe}_3)_2\}_3]$  have been reported ( $\text{Ln} = \text{Y, La, Pr, Nd, Sm, Er, and Lu}$  at present). The general synthetic route is:



These compounds have three-coordinate triangular pyramidal structures, similar to those found in the silylamides  $[\text{Ln}\{\text{N}(\text{SiMe}_3)_2\}_3]$ .

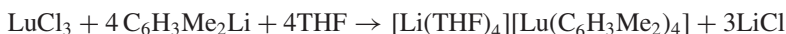
## 6.2.2 Aryls

Extended reaction at room temperature between powdered Ln ( $\text{Ln} = \text{Ho, Er, Tm, Lu}$ ) and  $\text{Ph}_2\text{Hg}$  in the presence of catalytic amounts of  $\text{LnI}_3$  affords the  $\sigma$ -aryls *fac*- $\text{LnPh}_3(\text{thf})_3$ . These have molecular structures with octahedral coordination of the lanthanides.



[Carrying out the reaction using Eu and Yb yields  $\text{EuPh}_2(\text{THF})_2$  and  $\text{YbPh}_2(\text{THF})_2$ , see Section 6.5.1.]

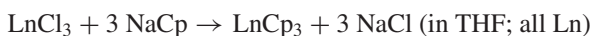
Using the bulkier 2,6-dimethylphenyl ligand results in  $[\text{Li}(\text{THF})_4]^+ [\text{Ln}(2,6\text{-Me}_2\text{C}_6\text{H}_3)_4]^-$  for the two smallest lanthanides, ytterbium (lemon) and lutetium (colourless).



## 6.3 Cyclopentadienyls

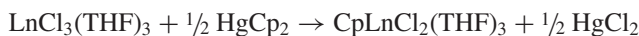
### 6.3.1 Compounds of the Unsubstituted Cyclopentadienyl Ligand ( $\text{C}_5\text{H}_5 = \text{C}_p$ ; $\text{C}_5\text{Me}_5 = \text{C}_p^*$ )

Cyclopentadienyl (and substituted variants thereof) has been the most versatile ligand used in organolanthanide chemistry. Unlike the situation with the d-block metals, where a maximum of two pentahapto- ( $\eta^5$ -)cyclopentadienyls can coordinate, up to three  $\eta^5$ -cyclopentadienyls can be found for the lanthanides, in keeping with the higher coordination numbers found for the f-block elements. In terms of the space occupied, a  $\eta^5$ -cyclopentadienyl takes up three sites in the coordination sphere. Three types of compound can be obtained, depending upon the stoichiometry of the reaction mixture:

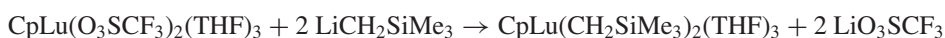


The mono(cyclopentadienyl) complexes all have pseudo-octahedral structures (Figure 6.2).

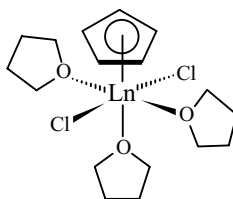
Another route for their synthesis is



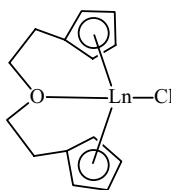
Cases are known of other anionic ligands present, and the triflate  $\text{CpLu}(\text{O}_3\text{SCF}_3)_2(\text{thf})_3$  can be used as a synthon for a dialkyl:



The structures of the two other families of compounds are more complicated. After synthesis,  $\text{LnCp}_2\text{Cl}$  are isolated by removal of the THF solvent, followed by vacuum sublimation.  $\text{LnCp}_2\text{Cl}$  tend to be associated, most usually as symmetric dimers  $[\text{Cp}_2\text{Ln}(\mu\text{-Cl})_2\text{LnCp}_2]$ , but  $\text{DyCp}_2\text{Cl}$  has a polymeric chain structure and  $\text{GdCp}_2\text{Cl}$  is a tetramer. These compounds can be isolated only for Gd–Lu and Y, the smaller lanthanides, for the unsubstituted cyclopentadienyl ring, but, with the bulkier  $\text{Cp}^*$  ligands,  $[\text{Cp}^*_2\text{Ln}(\mu\text{-Cl})_2\text{LnCp}^*_2]$  are obtainable for metals like La as well. A few other systems like  $\text{LnCp}_2\text{X}$  ( $\text{X} = \text{Br}, \text{I}$ ) have also been made.

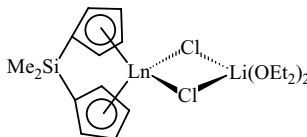


**Figure 6.2**  
Structure of  $\text{CpLnCl}_2(\text{THF})_3$ .

**Figure 6.3**

Structure of  $[\{O(CH_2CH_2C_5H_4)_2\}LnCl]$ .

Adducts  $[Cp^*_2LnCl(thf)]$  have been isolated from THF solutions for most lanthanides and a number of other  $[Cp_2LnCl(thf)]$  have been made. (The THF can be replaced by other Lewis bases such as MeCN and CyNC (Cy = cyclohexyl), whilst the chloride ligand may be substituted too.) Under some circumstances, the product of synthesis is a species like the remarkable blue, pentane-soluble ‘ate’ complex,  $[Cp^*_2Nd(\mu-Cl)_2Li(thf)_2]$ . Another way of obtaining bis(cyclopentadienyl) complexes is to link the two rings. If the link is functionalized with a donor atom, coordinative saturation can be achieved without solvent coordination (Figure 6.3) and without the formation of an ‘ate’ complex, which might otherwise be obtained (Figure 6.4).

**Figure 6.4**

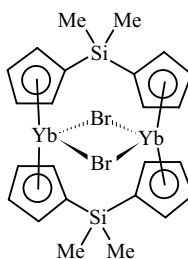
Structure of  $[\{Me_2Si(C_5H_4)_2\}Ln(\mu-Cl)_2Li(OEt_2)_2]$ .

Cases are known where these ligands bridge two metals, instead of chelating (Figure 6.5).

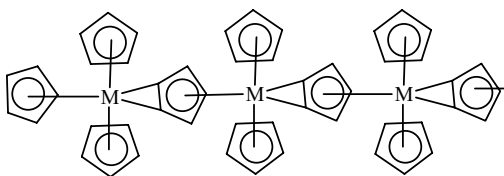
Tris(cyclopentadienyl) compounds  $Ln(C_5H_5)_3$  are isolated from synthesis in THF as adducts  $[Ln(C_5H_5)_3(THF)]$  (see below, this Section, and Figure 6.7), which undergo vacuum sublimation to afford pure  $Ln(C_5H_5)_3$ . These compounds are thermally stable but air- and moisture-sensitive, and are labile enough to react rapidly with  $FeCl_2$ , forming ferrocene. Their coordination spheres are unsaturated, to judge by their readiness to form adducts with Lewis bases like THF, RNC, RCN, and pyridine, and also by their solid-state structures.

The structures of  $Ln(C_5H_5)_3$  are shown in Figure 6.6. The coordination number of the metal increases with increasing size of the lanthanide. Assuming that an  $\eta^5-C_5H_5$  group occupies three coordination sites, then only ytterbium forms a simple molecular ‘9 coordinate’  $[Yb(\eta^5-C_5H_5)_3]$ . The compounds of slightly larger metals like Y and Er associate through weak Van der Waals’ forces, affording a compound where the coordination number is slightly greater than 9. Early lanthanides form compounds where the metals additionally form some  $\eta^1$  and  $\eta^2$  interactions. At the other end of the series, lutetium is evidently too small to form three  $\eta^5$ -linkages. Coordination numbers of the lanthanides in these compounds are thus 11 for La and Pr, 10 for Nd, 9 (+) for Y, Er and Tm, 9 for Yb, and 8 for Lu. Compounds of the type  $Ln(C_5H_4R)_3$  can be made for substituted cyclopentadienyl ligands when R has little steric demand, but with bulky ligands this is frequently not possible.

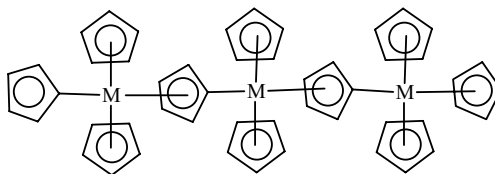
Adducts  $[Ln(C_5H_5)_3(THF)]$  exist for all lanthanides. They have ten-coordinate lanthanides with three  $\eta^5$ -cyclopentadienyl rings and a monodentate THF, having pseudo-tetrahedral geometry round the lanthanide (Figure 6.7). They are one of those rare cases when the same coordination number is maintained across the lanthanide series.

**Figure 6.5**Structure of  $[\{\text{He}_2\text{Si}(\text{C}_5\text{H}_4)_2\}_2 \text{Yb}_2 \text{Br}_2]$ .

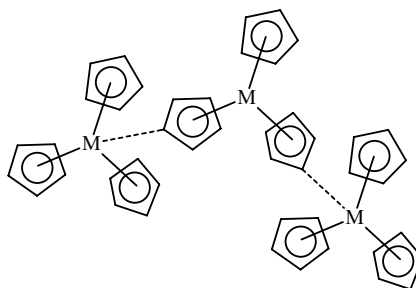
M = La, Pr



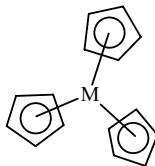
M = Nd



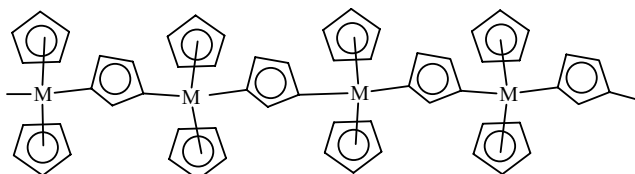
M = Y, Er, Tm

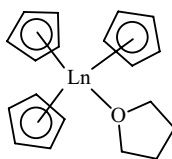


M = Yb



M = Lu

**Figure 6.6**Structures of  $\text{Ln}(\text{C}_5\text{H}_5)_3$ .

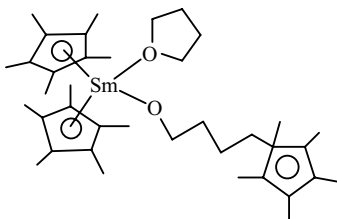
**Figure 6.7**

Structure of  $[\text{Ln}(\text{C}_5\text{H}_5)_3(\text{THF})]$ .

Other adducts whose structure has been confirmed by X-ray diffraction include  $[\text{La}(\text{C}_5\text{H}_5)_3(\text{NCMe})_2]$ ;  $[\text{Ln}(\text{C}_5\text{H}_5)_3(\text{NCEt})]$  ( $\text{Ln} = \text{La}, \text{Pr}, \text{Yb}$ );  $[\text{Pr}(\text{C}_5\text{H}_5)_3(\text{CNCy})]$ ; and  $[\text{Ln}(\text{C}_5\text{H}_5)_3(\text{py})]$  ( $\text{Ln} = \text{Nd}, \text{Sm}$ ).

### 6.3.2 Compounds $[\text{LnCp}^*_3]$ ( $\text{Cp}^* = \text{Pentamethylcyclopentadienyl}$ )

The  $\text{C}_5\text{Me}_5$  ligand is sterically more demanding than  $\text{C}_5\text{H}_5$ ;  $\text{C}_5\text{Me}_5$  also is more electron-donating than  $\text{C}_5\text{H}_5$ ; moreover, because it is more hydrocarbon-like,  $\text{C}_5\text{Me}_5$  ( $\text{Cp}^*$ ) complexes tend to be more hydrocarbon-soluble, another reason to use it for solution studies. Initially, work was concentrated on  $[\text{Cp}^*_2\text{Sm}(\text{THF})_2]$ , which led to extremely interesting chemistry (Section 6.5.2). Attempts to synthesize  $[\text{SmCp}^*_3]$  and other compounds of this type were unsuccessful, the obvious route such as the reaction between  $\text{SmCl}_3$  and  $\text{NaCp}^*$  in THF leading to ring-opened products (Figure 6.8).

**Figure 6.8**

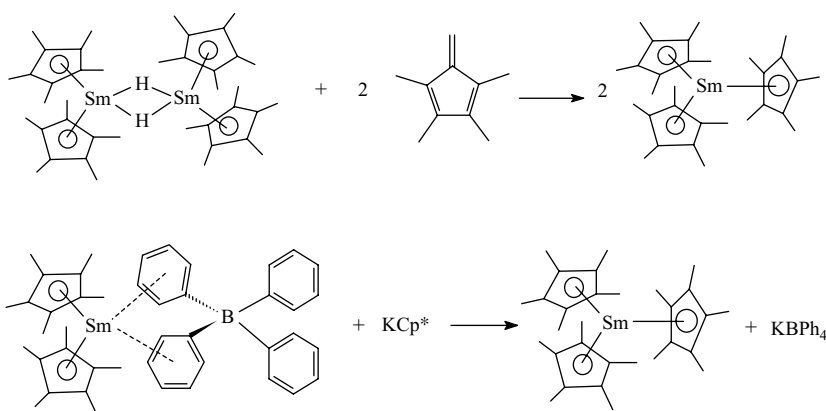
Structure of the ring-opened product of the reaction between  $\text{SmCl}_3$  and  $\text{NaCp}^*$  in THF.

In some remarkable work by W.J. Evans and his research group (W.J. Evans and B.L. Davis, *Chem. Rev.*, 2002, **102**, 2119), various syntheses have been developed which do not involve the use of THF, such as the reaction between tetramethylfulvene and a dimeric hydride, and the reaction of  $\text{KCp}^*$  with a cationic bis(pentamethylcyclopentadienyl) species (Figure 6.9).

The latter route has been applied to making all these compounds for La–Sm and Gd, as well as some even more congested molecules such as  $[\text{La}(\text{C}_5\text{Me}_4\text{R})_3]$  ( $\text{R} = \text{Et}, \text{SiMe}_3, \text{Pr}^i$ ). The difficulty in isolating the strongly oxophilic  $[\text{LnCp}^*_3]$  systems is such that synthesis conditions require not only the absence of Lewis bases such as THF, RNC, and RCN, all possibly donors, but in some cases required both the use of silylated glassware and the absence of even traces of THF vapour from gloveboxes used.

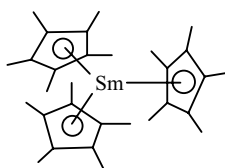
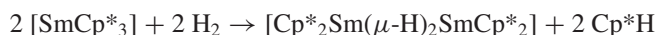
When  $[\text{SmCp}^*_3]$  was eventually isolated, it was found to be  $[\text{Sm}(\eta^5\text{-C}_5\text{Me}_5)_3]$  (Figure 6.10) and also that three of these bulky ligands fit round samarium with an increase in bond length from the usual 2.75 Å to 2.82 Å.

Apart from the novel ring-opening reaction with THF,  $[\text{LnCp}^*_3]$  inserts RNC and CO and is an ethene polymerization catalyst. Another reaction uncharacteristic of  $[\text{LnCp}_3]$  systems



**Figure 6.9**  
Routes for the synthesis of  $[\text{SmCp}^*_3]$ .

is its ready hydrogenolysis:



**Figure 6.10**  
Structure of  $[\text{SmCp}^*_3]$ .

### 6.3.3 Bis(cyclopentadienyl) Alkyls and Aryls $\text{LnCp}_2\text{R}$

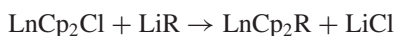
These compounds can be synthesized for the later lanthanides in particular. Reaction of  $\text{LnCp}_2\text{Cl}$  with  $\text{LiAlMe}_4$  gives a  $\mu$ -dimethyl-bridged species (Figure 6.11). Similar, but less stable, ethyls can also be made.



These heterometallic dimers undergo cleavage of the bridge with pyridine (Figure 6.12) to give  $[\text{LnCp}_2\text{R}]_2$ .

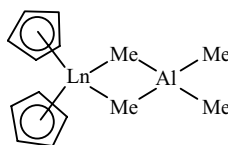


Similarly, reactions of  $\text{LiR}$  with  $\text{LnCp}_2\text{Cl}$  {which, strictly, should be written to give the product  $[\text{Cp}_2\text{Ln}(\mu\text{-Cl})_2\text{LnCp}_2]$ } resulted in the synthesis of  $\text{LnCp}_2\text{R}$  (R, e.g.,  $\text{Bu}^n$ ,  $\text{Bu}^t$ ,  $\text{CH}_2\text{SiMe}_3$ ,  $p\text{-C}_6\text{H}_4\text{Me}$ , etc.) for later lanthanides:



When this reaction is carried out in THF, a solvent that can coordinate well, the product is  $\text{LnCp}_2\text{R}(\text{THF})$ .



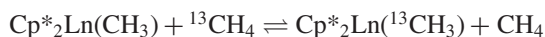


**Figure 6.11**  
Structure of  $[\text{Cp}_2\text{Ln}(\mu\text{-Me}_2) \text{AlMe}_2]$ .

### 6.3.4 Bis(pentamethylcyclopentadienyl) Alkyls

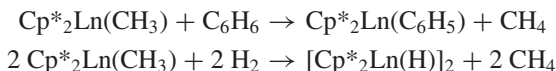
The extra bulk of the  $\text{C}_5\text{Me}_5$  ligand increases the possibility of crowding in these compounds.  $\text{Cp}^*_2\text{LnR}(\text{THF})$  systems are less stable than the corresponding  $\text{Cp}_2\text{LnR}(\text{THF})$ .  $[\text{Cp}^*_2\text{Ln}\{\text{CH}(\text{SiMe}_3)_2\}]$  are obtained THF-free, and even exhibit an agostic interaction between the lanthanide and one of the methyl carbons (Figure 6.13). The agostic  $\text{Ln} \cdots \text{C}$  distance also decreases with increasing atomic number (size). The interaction is too weak to be seen on the NMR timescale.

$\text{Cp}^*_2\text{Ln}(\text{CH}_3)$  is a remarkable compound. In the solid state, it is an unsymmetrical dimer (Figure 6.14), but in solution this is in equilibrium with the monomer. Monomeric  $\text{Cp}^*_2\text{Ln}(\text{CH}_3)$  undergoes some remarkable reactions with inert substances, demonstrating a very high Lewis acidity. Thus it activates  $\text{CH}_4$ , a reaction that can be followed using isotopically labelled methane.



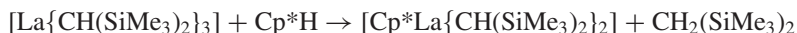
A possible mechanism is shown in Figure 6.15. The mechanism shown above is bimolecular, involving association. An alternative, that does not involve initial coordination of methane, is shown in Figure 6.16.

$\text{Cp}^*_2\text{Ln}(\text{CH}_3)$  also activates benzene, and readily undergoes hydrogenolysis:



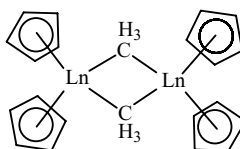
It undergoes ready insertion of alkenes into the  $\text{Ln}-\text{C}$  bond and is a very active catalyst for the polymerization of ethene.

Some compounds are known with just one Cp-type ligand (Figure 6.17).

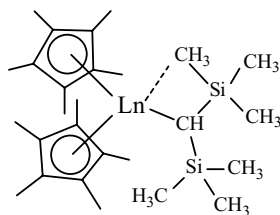


It features agostic interactions with two methyl groups; if the lanthanum atom were just bound to an  $\eta^5$ -cyclopentadienyl and also formed two  $\sigma$ -bonds to alkyl groups, it would be regarded as five coordinate and thus coordinatively unsaturated and electron-deficient. The agostic interactions relieve this.

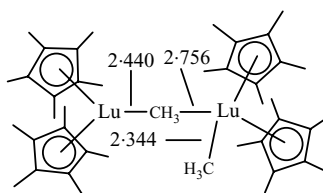
Another mono(pentamethylcyclopentadienyl) alkyl is  $[\text{Li}(\text{tmed})_2][\text{Cp}^*\text{LuMe}_3]$ .



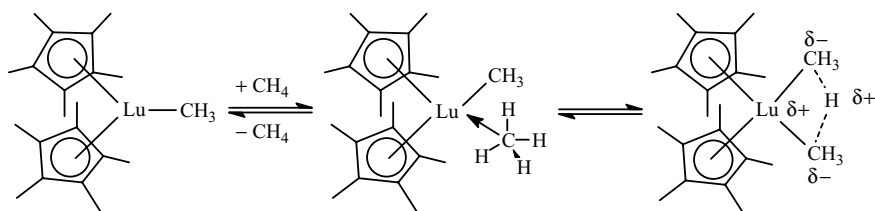
**Figure 6.12**  
Structure of  $[\text{Cp}_2\text{Ln}(\mu\text{-Me}_2) \text{LnCp}_2]$ .



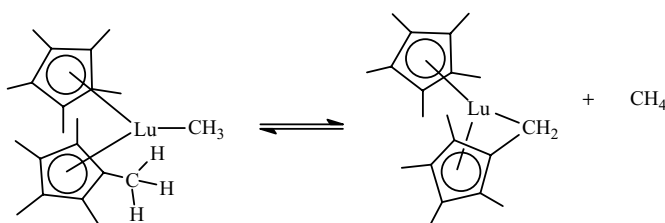
**Figure 6.13**  
Structure of  $[\text{Cp}^*_2\text{Ln}\{\text{CH}(\text{SiMe}_3)_2\}]$ .



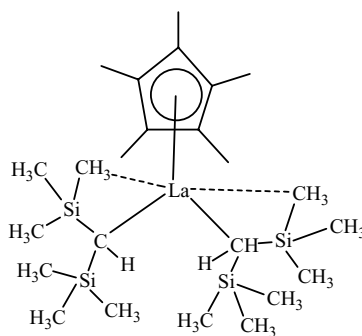
**Figure 6.14**  
Structure of  $[\text{Cp}^*_2\text{Lu}(\mu\text{-Me})\text{LuCp}^*_2\text{Me}]$ .



**Figure 6.15**  
Reaction of  $[\text{Cp}^*_2\text{LuMe}]$  with  $\text{CH}_4$ .



**Figure 6.16**  
Intramolecular elimination of methane from  $[\text{Cp}^*_2\text{LuMe}]$ .



**Figure 6.17**  
Structure of  $[\text{Cp}^*\text{La}\{\text{CH}(\text{SiMe}_3)_2\}_2]$ .

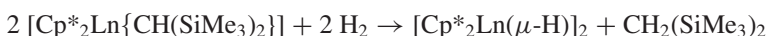
$\text{LuCl}_3 + \text{NaCp}^* + 2 \text{ TMED} + 3 \text{ LiMe} \rightarrow [\text{Li}(\text{tmed})_2] [\text{Cp}^*\text{LuMe}_3] + \text{NaCl} + 2 \text{ LiCl}$ .  
The  $[\text{Cp}^*\text{LuMe}_3]^-$  anion has a piano-stool structure with some asymmetry in the reported Lu–C distances of 2.39(2), 2.56(2), and 2.59(2) Å.

### 6.3.5 Hydride Complexes

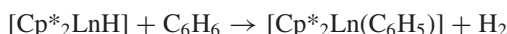
These can be made by various routes, including hydrogenolysis of Ln–C bonds; thermolysis of alkyls; and substitution of halide. Thus hydrogenolysis of the dimeric methyl-bridge cyclopentadienyl complexes (Ln, e.g., Y, Er, Yb, Lu) in THF affords  $[\text{Cp}_2\text{Ln}(\text{thf})(\mu\text{-H})]_2$ :



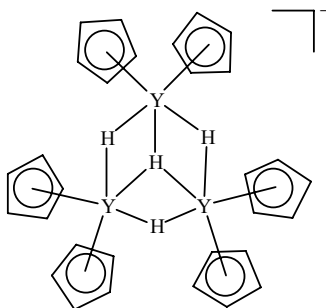
A similar reaction occurs in pentane at room temperature (Ln, e.g., Y, La–Nd, Sm, Lu):



The hydride group in these compounds can be very reactive:



Other hydrides are trinuclear, such as the anion  $[\{\text{Cp}_2\text{Y}(\mu_2\text{-H})\}_3(\mu_3\text{-H})]^-$  (Figure 6.18). It is formed by the reaction of  $[\text{Cp}_2\text{Y}(\mu\text{-Me})]_2$  with hydrogen in the presence of LiCl.



**Figure 6.18**  
Structure of  $[\{\text{Cp}_2\text{Y}(\mu_2\text{-H})\}_3(\mu_3\text{-H})]^-$ .

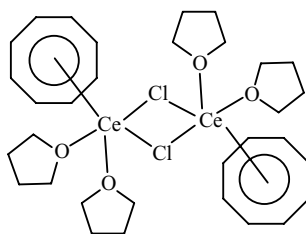
Reduction of  $[\text{Cp}_2\text{LuCl}(\text{THF})]$  with Na/THF gives a similar trinuclear species,  $[\text{Na}(\text{THF})_6] [\{\text{Cp}_2\text{Lu}(\mu_2\text{-H})\}_3(\mu_3\text{-H})]$ .

## 6.4 Cyclooctatetraene Dianion Complexes

Just as  $\text{C}_5\text{H}_5^-$  and its analogues are aromatic 6-electron ligands, the cyclooctatetraene dianion,  $\text{C}_8\text{H}_8^{2-}$ , is an aromatic 10-electron ligand. Several types of complex have been obtained. The product of the reaction between  $\text{LnCl}_3$  and  $\text{K}_2\text{C}_8\text{H}_8$  in THF depends upon stoichiometry:



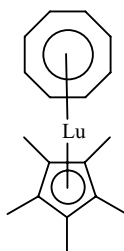
Both compounds have been obtained for most lanthanides. The anion in  $\text{K}(\text{dme})_2 [\text{Ln}(\text{C}_8\text{H}_8)_2]$  has a ‘uranocene’-like sandwich structure (Section 13.7), whilst  $[(\text{C}_8\text{H}_8)\text{Ce}(\text{THF})_2\text{Cl}]_2$  has a dimeric structure with bridging chlorides (Figure 6.19). All



**Figure 6.19**  
Structure of dimeric  $[(C_8H_8)Ce(THF)_2Cl]_2$ .

these compounds seem essentially ‘ionic’, reacting with  $UCl_4$  to form  $[U(C_8H_8)_2]$  quantitatively.

Co-condensation of the metal vapour and cyclooctatetraene at 77 K gives  $Ln_2(C_8H_8)_3$  ( $Ln$ , e.g., Ce, Nd, Er); crystallization from THF gives  $[(C_8H_8)Ln(THF)_2][Ln(C_8H_8)_2]$ . Mixed-ring complexes  $[(C_8H_8)Ln(Cp)(THF)_n]$  can be made by routes such as equimolar amounts of  $[(C_8H_8)Ln(THF)Cl]$  and NaCp or  $[CpLnCl_2(THF)_3]$  with  $K_2C_8H_8$ , though ‘one-pot’ routes work equally as well. Unsolvated complexes would be coordinatively unsaturated, hence the coordinated THF, as in  $[(C_8H_8)Pr(C_5H_5)(THF)_2]$  and  $[(C_8H_8)Y(C_5H_4Me)(THF)]$ , but use of bulky substituted cyclopentadienyl gives unsolvated compounds like  $[(C_8H_8)Lu\{C_5(CH_2Ph)_5\}]$  and  $[(C_8H_8)LuCp^*]$  (Figure 6.20).



**Figure 6.20**  
Structure of  $[(C_8H_8)LuCp^*]$ .

## 6.5 The +2 State

### 6.5.1 Alkyls and Aryls

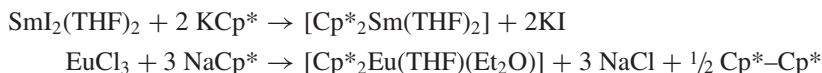
A number of simple alkyls and aryls have been made. The use of a bulky silicon-substituted *tert*-butyl ligand permitted the isolation of simple monomeric (bent) alkyls  $[Ln\{C(SiMe_3)_3\}_2]$  ( $Ln = Eu, Yb$ ) which are easily sublimeable *in vacuo*. Unlike lanthanide cyclopentadienyls, it is very rare for simple  $\sigma$ -bonded organolanthanides to be stable enough to be sublimeable *in vacuo*. Evidently the very bulky organic ligands enclose the metal ions very well, so that the intermolecular forces are essentially weak Van der Waals’ interactions between the organic groups, ensuring the molecules are volatile at low temperatures. Other such compounds include  $[Yb\{C(SiMe_3)_2(SiMe_2X)\}]$  ( $X = CH=CH_2; CH_2CH_2OEt$ ) and Grignard analogues  $[Yb\{C(SiMe_3)_2(SiMe_2X)\}I.OEt_2]$  ( $X = Me, CH=CH_2, Ph, OMe$ ), synthesized from RI and Yb. The alkylytterbium iodides have iodo-bridged dimeric structures, containing four-coordinate ytterbium when  $X = Me$ , but five coordinate for  $X = OMe$ , due to chelation.

Reaction of powdered Ln (Ln = Eu, Yb) and Ph<sub>2</sub>Hg in the presence of catalytic amounts of LnI<sub>3</sub> affords the compounds LnPh<sub>2</sub>(THF)<sub>2</sub>. The pentafluorophenyl [Eu(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(THF)<sub>5</sub>] has the pentagonal bipyramidal coordination geometry familiar for simple coordination compounds. Using a very bulky aryl ligand, Dpp (Dpp = 2,6-Ph<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), results in the isolation of [Ln(Dpp)I(THF)<sub>3</sub>] and [Ln(Dpp)<sub>2</sub>(THF)<sub>2</sub>] (Ln = Eu, Yb). In [Yb(Dpp)<sub>2</sub>(THF)<sub>2</sub>] the geometry is a strongly distorted tetrahedron; there are additionally two weak  $\eta^1 - \pi$ -arene interactions (Yb–C 3.138 Å) involving  $\alpha$ -carbons of the terphenyl groups. Structures are not yet known for LnPh<sub>2</sub>(THF)<sub>2</sub> (Ln = Eu, Yb); a coordination number of four seems low, as these are not bulky ligands. Possibly they may not have monomeric structures, or there are agostic interactions involving Ln...H–C bonding.

### 6.5.2 Cyclopentadienyls

Simple cyclopentadienyls [MCp<sub>2</sub>] (M = Eu, Yb) can be made by reaction of cyclopentadiene with solutions of the metal in liquid ammonia. The initial products are ammines [MCp<sub>2</sub>(NH<sub>3</sub>)<sub>x</sub>], which can be desolvated by heating *in vacuo*. [SmCp<sub>2</sub>] is also known. These compounds have been little studied on account of their low solubilities; using instead the pentamethylcyclopentadienyl group confers greater solubility in aromatic hydrocarbons like toluene.

Synthetic routes include:



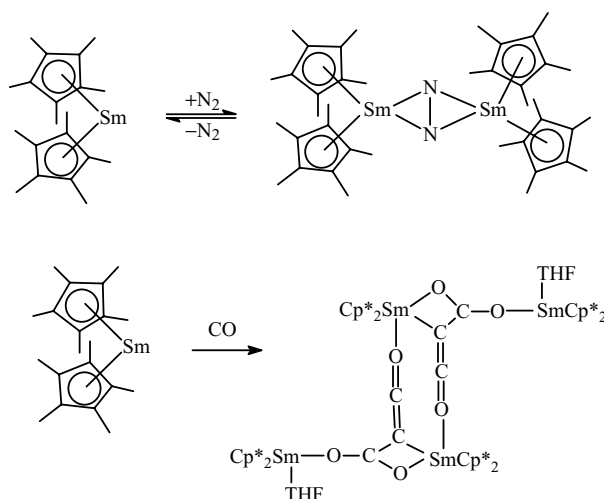
These compounds often desolvate readily, thus recrystallization of these two compounds from toluene gives [Cp\*<sub>2</sub>Ln(THF)] (Ln = Sm, Eu). Gentle heating of [Cp\*<sub>2</sub>Sm(THF)] *in vacuo* forms [Cp\*<sub>2</sub>Sm]. Whilst it is to be expected that [Cp\*<sub>2</sub>Ln(THF)<sub>n</sub>] will have bent structures, the angle between the planes of the Cp\* rings in crystals of [Cp\*<sub>2</sub>Ln] is 130–140°. It has been suggested that a bent molecule is polarized and can give stronger dipole–dipole forces attracting it to neighbouring molecules in the solid state. However, this is not the whole story, as electron diffraction results indicate an angle of 160° in the gas phase, and another possibility is that intramolecular nonbonded interactions are influential.

Besides forming adducts with Lewis bases (THF, Et<sub>2</sub>O, Ph<sub>3</sub>PO, etc.), [Cp\*<sub>2</sub>Sm] exhibits some remarkable reactions with dinitrogen (reversible) and carbon monoxide (irreversible) (Figure 6.21).

### 6.5.3 Other Compounds

Simple ‘cyclooctatetraenediyls’ [M(C<sub>8</sub>H<sub>8</sub>)] (M = Eu, Yb) can be made by reaction of cyclooctatetraene with solutions of the metal in liquid ammonia. Another route to [M(C<sub>8</sub>H<sub>8</sub>)] (Sm, Yb) is the reaction of the metals with cyclooctatetraene using iodine as catalyst. These compounds are not monomers, but the Lewis base adduct [M(C<sub>8</sub>H<sub>8</sub>)(py)<sub>3</sub>] has a ‘piano-stool’ structure.

Reaction of cyclooctatetraene with solutions of ytterbium and 2 moles of potassium in liquid ammonia gives K<sub>2</sub> [M(C<sub>8</sub>H<sub>8</sub>)<sub>2</sub>]; the solvate [K(dme)]<sub>2</sub> [Yb(C<sub>8</sub>H<sub>8</sub>)<sub>2</sub>] (DME = 1,2-dimethoxyethane) has a sandwich uranocene-type structure for the anion.

**Figure 6.21**

Products of the reaction of  $[\text{SmCp}^*_2]$  with  $\text{N}_2$  and  $\text{CO}$ .

## 6.6 The +4 State

Few compounds are known in this state, confined to  $\text{Ce}^{\text{IV}}$ ; even so, the oxidizing power of  $\text{Ce}^{\text{IV}}$ , together with the tendency for species like  $\text{LiR}$  or  $\text{NaR}$  to be reducing, makes these rare. Alkoxides  $[\text{Cp}_3\text{Ce}(\text{OR})]$  ( $\text{R} = \text{Pr}^i, \text{Bu}^t$ ) and  $[\text{Cp}_2\text{Ce}(\text{OBu}^t)_2]$  have been synthesized. One such route is:

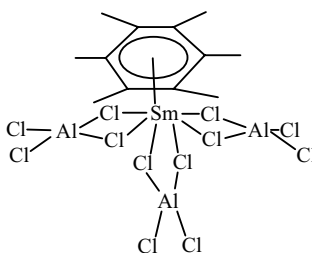


This uses an organotin compound as it is a weaker reducing agent than the alkali metal compounds usually used, and so less likely to result in reduction to  $\text{Ce}^{\text{III}}$ . The other compounds with claims to be in this oxidation state are  $[\text{Ce}(\text{C}_8\text{H}_8)_2]$  and analogues.  $[\text{Ce}(\text{C}_8\text{H}_8)_2]$  can be prepared by a ‘witches’ brew’ approach from a mixture of  $[\text{Ce}(\text{OPr}^i)_4(\text{Pr}^i\text{OH})]$ ,  $\text{AlEt}_3$ , and cyclooctatetraene at  $140^\circ\text{C}$ , or by  $\text{AgI}$  oxidation of  $\text{K}[\text{Ce}(\text{C}_8\text{H}_8)_2]$ ; the latter reaction can be reversed using metallic potassium as the reducing agent. Spectroscopic evidence support the view that this compound is  $[\text{Ce}^{3+}\{(\text{C}_8\text{H}_8)_2\}^{3-}]$  rather than  $[\text{Ce}^{4+}(\text{C}_8\text{H}_8^{2-})_2]$ . The related  $[\text{Ce}\{1,3,6-(\text{Me}_3\text{Si})_3\text{C}_8\text{H}_5\}_2]$ , more stable and more hydrocarbon-soluble, has also been synthesized.

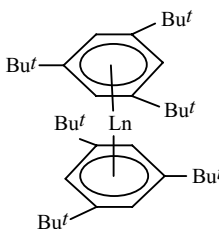
## 6.7 Metal–Arene Complexes

A few of these have been made in which lanthanides are refluxed with arenes under Friedel–Crafts conditions, such as  $[(\text{C}_6\text{Me}_6)\text{Sm}(\text{AlCl}_4)_3]$  (Figure 6.22). These appear to have the lanthanide in ‘normal’ oxidation states; the arene group is bound  $\eta^6$ . Interactions between a lanthanide and an arene ring are also well-authenticated in what would otherwise be coordinatively unsaturated aryloxides, like  $[\text{Yb}(\text{OC}_6\text{H}_3\text{Ph}_2)_3]$ .

A different type of compound (Figure 6.23) has been made by co-condensation of vapourized lanthanide atoms with 1,3,5-tri-*t*-butylbenzene at 77 K. These compounds are thermally stable for many lanthanides at room temperature and above, and are strongly coloured,



**Figure 6.22**  
Structure of  $[(C_6Me_6)Sm(AlCl_4)_3]$ .



**Figure 6.23**  
Structure of lanthanide bis(1,3,5-tri-*t*-benzene) compound.

pentane-soluble solids (the yttrium and gadolinium compounds, for example, can be sublimed at  $100\text{ }^{\circ}\text{C}/10^{-4}$  mbar with only partial decomposition).

The compounds of Nd, Gd–Er, Lu, and Y are stable to around  $100\text{ }^{\circ}\text{C}$ ; the La, Pr, and Sm compounds decompose at 0, 40 and  $-30\text{ }^{\circ}\text{C}$ , respectively. The compounds of Ce, Eu, Tm, and Yb could not be isolated. This cannot be explained simply by steric effects or redox behaviour of the metals; (i) compounds can be isolated with quite large early metals (Nd, Gd) but not with small ones like Yb; (ii) the compounds formally involve metals in the (0) state, so metals like Eu and Yb would have been expected to be successful in supporting low oxidation states. Steric factors may have their place, as the compounds of the earlier lanthanides (La–Pr) are less stable than might be expected, possibly because the ligands may not be bulky enough to stabilize the lanthanide atom against decomposition pathways.

This pattern is irregular but has been correlated with the  $f^n s^2 \rightarrow f^{n-1} d^1 s^2$  promotion energies, as it is believed that an accessible  $d^1 s^2$  configuration is necessary for stable bonding. A bonding model has been developed similar to that used for compounds like dibenzenechromium, requiring delocalization of metal  $e_{2g}$  electrons onto the aromatic rings. Bond dissociation energies have been measured in the range of 200–300 kJ/mole, and are quite comparable with known bis(arene) complexes of transition metals.

## 6.8 Carbonyls

One area which demonstrates the contrast between the lanthanides and the d-block transition metals is the absence of stable carbonyls. Co-condensation of the vapours of several metals (Pr, Nd, Eu, Gd, Ho, Yb) with CO in argon matrices at 4 K leads to compounds identified as  $[Ln(CO)_x]$  ( $x = 1-6$ ) from their IR spectra. They decompose on warming above 40 K.

Other compounds containing carbonyl groups are known, involving a transition metal. Most of these feature isocarbonyl linkages. Thus  $[\text{Cp}^*_2\text{Yb}]$  reacts with  $\text{Co}_2(\text{CO})_8$  in THF solution to form  $[\text{Cp}^*_2\text{Yb}(\text{THF})\text{-O-C-Co}(\text{CO})_3]$ . A few compounds actually contain metal-metal bonds involving a lanthanide, thus:



The Lu–Ru bond length is 2.966 Å.

**Question 6.1** Suggest why  $[\text{Li}(\text{L-L})]_3 [\text{Eu}(\text{CH}_3)_6]$  cannot be isolated.

**Answer 6.1** Europium is the lanthanide with the most stable divalent state, so reduction to a  $\text{Eu}^{\text{II}}$  compound is taking place.

**Question 6.2** Predict the coordination geometry of  $[\text{Ln}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2]$ .

**Answer 6.2** Trigonal bipyramidal, as with main group  $\text{AX}_5$  species. This will be more stable (repulsions minimized) than a square pyramidal structure.

**Question 6.3**  $[\text{Yb}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2]$  can be made by reaction of ytterbium chips with  $\text{ICH}_2\text{SiMe}_3$  in THF. Would this route be suitable for  $[\text{Eu}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2]$ ?

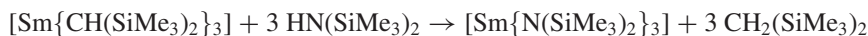
**Answer 6.3** Because of the high stability of the  $\text{Eu}^{\text{II}}$  state, it is possible that oxidation might only occur as far as a europium(II) species like  $[\text{Eu}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})_2]$ . The reaction does not seem to have been attempted yet.

**Question 6.4** Ether solutions of  $[\text{Lu}\{\text{CH}(\text{SiMe}_3)_2\}_3]$  react with  $\text{KX}$  ( $\text{X} = \text{Cl}, \text{Br}$ ), forming  $[(\text{Et}_2\text{O})\text{K}(\mu\text{-Cl})\text{Lu}\{\text{CH}(\text{SiMe}_3)_2\}_3]$ . This reaction is not shown by the lanthanum analogue. Comment on this.

**Answer 6.4** Lutetium is smaller than lanthanum, so would have a greater charge density and thus be a better electrophile, but this is still a surprising reaction. Coordination of the chloride to potassium and lutetium evidently compensates for the loss of lattice energy.

**Question 6.5** Chemically  $[\text{Ln}\{\text{CH}(\text{SiMe}_3)_2\}_3]$  behave as Lewis acids; besides reacting with water, like lanthanide organometallics in general, they also are attacked by other nucleophiles such as amines and phenols, forming the silylamides and aryloxides, respectively. Write equations for the reactions of  $[\text{Sm}\{\text{CH}(\text{SiMe}_3)_2\}_3]$  with  $\text{HN}(\text{SiMe}_3)_2$  and  $\text{HOC}_6\text{H}_2\text{Bu}_2^t\text{-2,6-Me-4}$ .

**Answer 6.5**  $[\text{Sm}\{\text{CH}(\text{SiMe}_3)_2\}_3] + 3 \text{HOC}_6\text{H}_2\text{Bu}_2^t\text{-2,6-Me-4} \rightarrow [\text{Sm}\{\text{OC}_6\text{H}_2\text{Bu}_2^t\text{-2,6-Me-4}\}_3] + 3 \text{CH}_2(\text{SiMe}_3)_2$



**Question 6.6** Comment on the formulae of the alkyls formed by the lanthanides with the  $\text{CH}_3$ ,  $\text{CH}_2\text{SiMe}_3$ ,  $\text{CMe}_3$  and  $\text{CH}(\text{SiH}_3)_2$  ligands (Section 6.2.1).

**Answer 6.6** The coordination number decreases from 6 in  $[\text{LnMe}_6]^{3-}$  through 5 and 4 in  $[\text{Ln}(\text{CH}_2\text{SiMe}_3)_3(\text{thf})_2]$ ,  $[\text{LnBu}_4']^-$  and  $[\text{Ln}(\text{CH}_2\text{SiMe}_3)_4]^-$  to 3 in  $[\text{Ln}\{\text{CH}(\text{SiH}_3)_2\}_3]$ , simply in order of the increasing bulk of the ligands, as hydrogens are replaced in the methyl group by  $\text{SiMe}_3$  groups.

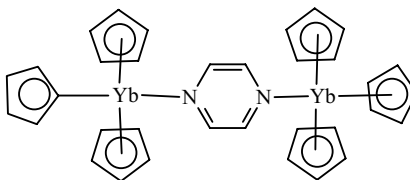
**Question 6.7**  $[\text{Cp}_2\text{LnCl}]$  are dimers in benzene solution but monomers in THF. Why?

**Answer 6.7** THF is a good Lewis base and cleaves the bridges, forming monomeric complexes  $[\text{Cp}_2\text{LnCl}(\text{THF})]$ . Benzene is too weak a donor to coordinate to the lanthanide.



**Question 6.8** Predict the structure of the complex formed between pyrazine (1,4-diazine) and  $[\text{Yb}(\text{C}_5\text{H}_5)_3]$ .

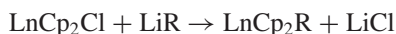
**Answer 6.8**  $[\{(\text{C}_5\text{H}_5)_3\text{Yb}\}(\text{pyrazine})\{\text{Yb}(\text{C}_5\text{H}_5)_3\}]$  (see Figure 6.24).



**Figure 6.24**

$[(\text{C}_5\text{H}_5)_3\text{Yb}(\mu\text{-pyrazine})\text{Yb}(\text{C}_5\text{H}_5)_3]$ .

$\text{LnCp}_2\text{R}$  (R e.g.  $\text{Bu}^n$ ,  $\text{Bu}^t$ ,  $\text{CH}_2\text{SiMe}_3$ ,  $p\text{-C}_6\text{H}_4\text{Me}$ , etc.) can be made for later lanthanides:



When this reaction is carried out in THF, the product is  $\text{LnCp}_2\text{R}(\text{thf})$  (Figure 6.15).

**[Question 6.9]** Structures of a number of lutetium alkyls  $\text{LuCp}_2\text{R}(\text{thf})$  have been examined by crystallographers. Some structural data are listed in Table 6.1; comment on there.

**Table 6.1** Bond lengths in some  $\text{Cp}_2\text{Lu}$  complexes

Compound	Lu–C (Å)	Lu–O (Å)
$\text{Cp}_2\text{Lu}(\text{Bu}^t)(\text{thf})$	2.47(2)	2.31(2)
$\text{Cp}_2\text{Lu}(\text{CH}_2\text{SiMe}_3)(\text{thf})$	2.376(17)	2.288(10)
$\text{Cp}_2\text{Lu}(p\text{-MeC}_6\text{H}_4)(\text{thf})$	2.345(39)	2.265(28)
$\text{Cp}_2\text{Lu}(\text{Cl})(\text{thf})$		2.27(1)

**Answer 6.9** Both the Lu–C  $\sigma$ -bond and Lu–O bond lengths in  $\text{LuCp}_2\text{Bu}^t(\text{thf})$  look unusually long in comparison with the other compounds, suggesting that there is steric crowding here.

**Question 6.10** The Lu–C  $\sigma$ -bond distance in  $[\text{Cp}_2\text{Lu}(\text{CH}_2)_3\text{NMe}_2]$  (Figure 6.25) is 2.22 (1) Å. Compare it with the compounds in the preceding question and comment on this.

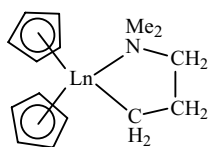
**Answer 6.10** The Lu–C distance in  $[\text{Cp}_2\text{Lu}(\text{CH}_2)_3\text{NMe}_2]$  is shorter than any of the others (it is the shortest Lu–C  $\sigma$ -bond reported) and must reflect an uncrowded environment around lutetium due to the presence of a chelate ring in place of two monodentate ligands.

**Question 6.11** Read Section 6.3.4 and predict the products of reaction of  $\text{Cp}^*_2\text{Ln}(\text{CH}_3)$  on gentle warming with  $\text{SiMe}_4$ , another ‘inert’ molecule.

**Answer 6.11**  $[\text{Cp}^*_2\text{Ln}(\text{CH}_2\text{SiMe}_3)_3] + \text{CH}_4$

**Question 6.12** Predict the products of reaction of  $[\text{Cp}^*_2\text{LnH}]$  with  $\text{Et}_2\text{O}$ .

**Answer 6.12**  $[\text{Cp}^*_2\text{Ln}(\text{OEt})]$  and  $\text{EtOH}$ .

**Figure 6.25**Structure of  $[(\text{Cp})_2\text{Lu}(\text{CH}_2)_3\text{NMe}_2]$ .

**Question 6.13** Why does using the pentamethylcyclopentadienyl group make these compounds more soluble?

**Answer 6.13** The  $\text{Cp}^*$  group on account of its bulk shields the metal more. It makes coordinative saturation more likely, so that there is less tendency to oligomerize, and the molecule presents a more 'organic' exterior to the solvent.

**Question 6.14** In many of its reactions  $[\text{Cp}^*_2\text{Sm}]$  is oxidized to  $\text{Sm}^{\text{III}}$  compounds. Suggest products of such reactions between THF solutions of  $[\text{Cp}^*_2\text{Sm}]$  and (i)  $\text{HgPh}_2$ , (ii)  $\text{Ag}^+ \text{BPh}_4^-$ , (iii)  $\text{C}_5\text{H}_6$ .

**Answer 6.14** (i)  $[\text{Cp}^*_2\text{SmPh}(\text{THF})]$ ; (ii)  $[\text{Cp}^*_2\text{Sm}(\text{THF})_2]^+ \text{BPh}_4^-$ ; (iii)  $[\text{Cp}^*_2\text{Sm}(\text{Cp})]$ .

**Question 6.15** Why do stable binary carbonyls of these metals not exist? (Consider what d-block transition metals need to do to form stable carbonyls that the lanthanides cannot do.)

**Answer 6.15** Transition metals need both vacant orbitals to accept electron pairs from the  $\sigma$ -donor (ligand) and also filled d orbitals for  $\pi$  back-donation (back-bonding) to the ligand (note that neither the very early nor the very late transition metals form stable binary carbonyls). CO is a rather weak  $\sigma$ -donor, and lanthanides tend to complex only with good  $\sigma$ -donors. For  $\pi$ -bonding to occur, the metal must possess suitable orbitals to  $\pi$ -bond to the ligands, and the 'inner' 4f orbitals are unsuited to this, unlike the  $d_{xy}$ ,  $d_{xz}$ , and  $d_{yz}$  orbitals of transition metals.



# 7 The Misfits: Scandium, Yttrium, and Promethium

By the end of this chapter you should be able to:

- recognize that yttrium resembles the later lanthanides in its chemistry;
- recall that scandium differs from both the transition metals and the lanthanides in its chemistry;
- appreciate that promethium is a typical lanthanide in the types of compounds it forms, despite its radioactivity and the difficulties posed to its study.

## 7.1 Introduction

Scandium and yttrium are elements in Group IIIA (3) of the Periodic Table, usually placed above La (or Lu). Their treatment is frequently grouped with the lanthanides in textbooks (often for reasons of convenience). Promethium is, however, a radioactive lanthanide not encountered in the vast majority of laboratories.

Both scandium and yttrium are electropositive metals with similar reduction potentials to the lanthanides ( $E^\circ \text{Sc}^{3+}/\text{Sc} = -2.03 \text{ V}$ ;  $E^\circ \text{Y}^{3+}/\text{Y} = -2.37 \text{ V}$ ; compare values of  $-2.37 \text{ V}$  and  $-2.30 \text{ V}$  for La and Lu, respectively). The ionic radii of  $\text{Sc}^{3+}$  and  $\text{Y}^{3+}$  are  $0.745 \text{ \AA}$  and  $0.900 \text{ \AA}$ , respectively (in six coordination). The former is much smaller than any  $\text{Ln}^{3+}$  ion but yttrium is very similar to  $\text{Ho}^{3+}$  (radius  $0.901 \text{ \AA}$ ); purely on size grounds, it would be predicted that yttrium would resemble the later lanthanides but that scandium would exhibit considerable differences, and this expectation is largely borne out in practice. Table 7.1 lists stability constants for typical complexes of  $\text{Sc}^{3+}$  and  $\text{Y}^{3+}$ , together with values for  $\text{La}^{3+}$  and  $\text{Lu}^{3+}$ .

## 7.2 Scandium

When Mendeleev produced his original Periodic Table in 1869, he left a space for a metallic element of atomic mass 44 preceding yttrium. The first fairly pure scandium compounds were isolated by Cleve in 1879, but it was not until 1937 that the element itself was isolated. Although a relatively abundant element, it is fairly evenly distributed in the earth's crust and has no important ores, though it is the main component of the rare ore thortveitite ( $\text{Sc}_2\text{Si}_2\text{O}_7$ ), thus being relatively expensive. In fact, it is mainly obtained as a by-product from uranium extraction.

**Table 7.1** Aqueous stability constants ( $\log \beta_1$ ) for complexes of Sc, Y, La and Lu

Ligand	I (mol/dm <sup>3</sup> )	Sc <sup>3+</sup>	Y <sup>3+</sup>	La <sup>3+</sup>	Lu <sup>3+</sup>
F <sup>−</sup>	1.0	6.2 <sup>a</sup>	3.60	2.67	3.61
Cl <sup>−</sup>	1.0	0	−0.1	−0.1	−0.4
Br <sup>−</sup>	1.0	−0.1	−0.15	−0.2	
NO <sub>3</sub> <sup>−</sup>	1.0	0.3		0.1	−0.2
OH <sup>−</sup>	0.5	9.3*	5.4	4.7	5.8
acac <sup>−</sup>	0.1	8.00	5.89	4.94	6.15
EDTA <sup>4−</sup>	0.1	23.1	18.1	15.46	19.8
DTPA <sup>5−</sup>	0.1	24.4	22.4	19.5	22.4
OAc <sup>−</sup>	0.1		1.68	1.82	1.85

<sup>a</sup> = Data for solutions of slightly different ionic strength.

Scandium is a soft and silvery metal; it is electropositive, tarnishing rapidly in air and reacting with water. It is generally obtained by chemical reduction, for example the reaction of the trifluoride with calcium. It has only one natural isotope, <sup>45</sup>Sc.

### 7.2.1 Binary Compounds of Scandium

Scandium oxide, Sc<sub>2</sub>O<sub>3</sub>, is a white solid (mp 3100 °C; Mn<sub>2</sub>O<sub>3</sub> structure) made by burning the metal or by heating compounds such as the hydroxide or nitrate. It has a bcc structure with 6-coordinate scandium and has amphoteric properties, dissolving in alkali as [Sc(OH)<sub>6</sub>]<sup>3−</sup> ions. All four scandium(III) halides are known, all but the fluoride (WO<sub>3</sub> structure) having the FeCl<sub>3</sub> structure. All are white solids. They can be obtained directly from the elements and in some cases by dehydration of the hydrated salts as well as by thermal decomposition of (NH<sub>4</sub>)<sub>3</sub>ScX<sub>6</sub> (X = Cl, Br), a method also used for the lanthanides. Other significant binary compounds include the fcc dihydride ScH<sub>2</sub>; unlike most of the lanthanides, scandium does not form a trihydride.

Scandium forms a number of well-defined lower halides, especially chlorides. These are synthesized by high-temperature reaction of Sc with ScCl<sub>3</sub>. They include ScCl, Sc<sub>2</sub>Cl<sub>3</sub> ('mouse fur'), Sc<sub>5</sub>Cl<sub>8</sub>, Sc<sub>7</sub>Cl<sub>10</sub>, and Sc<sub>7</sub>Cl<sub>12</sub>. They typically have chain structures with metal–metal bonding and octahedral clusters of scandium atoms. ScCl is isostructural with ZrBr, Sc<sub>5</sub>Cl<sub>8</sub> contains infinite chains of Sc<sub>6</sub> octahedra sharing trans-edges, whilst Sc<sub>7</sub>Cl<sub>10</sub> has two parallel chains of octahedra sharing a common edge. Sc<sub>7</sub>Cl<sub>12</sub> is regarded as made of Sc<sub>6</sub>Cl<sub>12</sub> octahedra with isolated scandium atoms in octahedral interstices. Sc<sub>2</sub>Br<sub>3</sub> is also known.

## 7.3 Coordination Compounds of Scandium

As already mentioned, the ionic radius of Sc<sup>3+</sup> is, at 0.745 Å (for 6-coordination), the largest of the metals in its period, so that high coordination numbers are frequently met with in its chemistry; examples between 3 and 9 are known. <sup>45</sup>Sc has *I* = 7/2 and a few NMR studies are being reported.

### 7.3.1 The Aqua Ion and Hydrated Salts

For many years it was assumed that, like the succeeding d-block metals, scandium formed a [Sc(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup> ion. Various pieces of evidence indicated this was not the case – salts containing dimeric [(H<sub>2</sub>O)<sub>5</sub>Sc(OH)<sub>2</sub>Sc(H<sub>2</sub>O)<sub>5</sub>]<sup>4+</sup> ions with approximately pentagonal

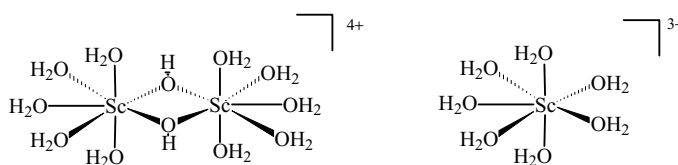


Figure 7.1

bipyramidal seven coordination of scandium were crystallized (Figure 7.1); EXAFS spectra of solutions indicated an Sc–O distance (2.180 Å) longer than that expected for octahedral coordination (2.10–2.12 Å) but in keeping with values obtained for the seven-coordinate scandium ion described above; Raman spectra of aqueous solutions were inconsistent with octahedral  $[\text{Sc}(\text{H}_2\text{O})_6]^{3+}$  ions; size considerations suggested seven coordination. Finally, several salts  $[\text{Sc}(\text{H}_2\text{O})_7] \text{X}_3$  were obtained [ $\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{and } \text{C}(\text{O}_2\text{SCF}_3)_3$ ] which contain (roughly) pentagonal bipyramidal  $[\text{Sc}(\text{H}_2\text{O})_7]^{3+}$  ions (Figure 7.1) with Sc–O of 2.18–2.19 Å.

Table 7.2 gives the coordination numbers in aqueous solution of a number of  $[\text{M}(\text{H}_2\text{O})_n]^{3+}$  ions, together with their ionic radii (for six coordination, for a fair comparison of size), showing why  $\text{Sc}^{3+}$  might have been predicted to form a seven-coordinate aqua ion, purely on grounds of size.

A range of solid hydrated salts has been isolated and some structures are known. In addition to the seven-coordinate  $[\text{Sc}(\text{H}_2\text{O})_7] \text{X}_3$  [ $\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{and } \text{C}(\text{O}_2\text{SCF}_3)_3$ ],  $\text{Sc}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$  contains  $[\text{Sc}(\text{H}_2\text{O})_6]^{3+}$  ions and the triflate  $\text{Sc}(\text{O}_3\text{SCF}_3)_3 \cdot 9\text{H}_2\text{O}$  has  $[\text{Sc}(\text{H}_2\text{O})_9]^{3+}$  ions – as with the lanthanides (ions with these unusual coordination numbers are stabilized in the solid state by hydrogen-bonding). There are also  $\text{Sc}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$  and  $\text{Sc}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ . The structure of the nitrate is not known, but it should be noted that eight- and nine-coordinate  $\text{Sc}(\text{NO}_3)_3(\text{H}_2\text{O})_2$  and  $\text{Sc}(\text{NO}_3)_3(\text{H}_2\text{O})_3$  molecules are present in crown ether complexes.

### 7.3.2 Other Complexes

Scandium forms conventional halide complexes, like the hexafluoroscandates  $\text{M}_3\text{ScF}_6$  which clearly contain  $[\text{ScF}_6]^{3-}$  anions, such as  $\text{Na}_3\text{ScF}_6$ ; other octahedral anions are found in  $\text{Na}_3\text{ScCl}_6$  (cryolite structure),  $\text{Cs}_2\text{LiScCl}_6$  (elpasolite structure), and  $\text{Na}_3\text{ScBr}_6$ . Six coordination is the norm; however, a Raman study of  $\text{CsCl}-\text{ScCl}_3$  melts in the range 600–900 °C indicates that though the main species present is  $[\text{ScCl}_6]^{3-}$  ( $\nu \text{ Sc}-\text{Cl } 275 \text{ cm}^{-1}$ ) there is evidence for the species  $[\text{ScCl}_7]^{4-}$  ( $\nu \text{ Sc}-\text{Cl } 260 \text{ cm}^{-1}$ ).

A range of O-donor ligands (e.g. THF,  $\text{Me}_2\text{SO}$ ,  $\text{R}_3\text{PO}$ ) forms complexes with scandium, with two main series,  $\text{ScL}_3\text{X}_3$  (where X is a coordinating anion like chloride) and  $\text{ScL}_6\text{X}_3$  (with anions like perchlorate); however, at the moment, very few structures are confirmed. Six coordination is confirmed for *mer*- $\text{Sc}(\text{THF})_3\text{Cl}_3$ , which reacts with a small amount of

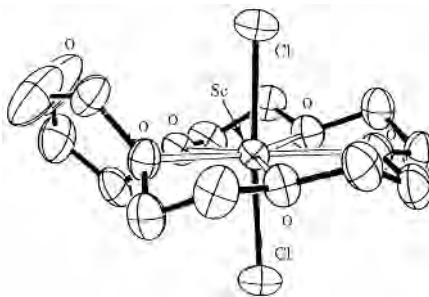
Table 7.2

$\text{M}^{3+}$ ion	Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy
Ionic radius (Å)	0.745	0.900	1.032	1.01	0.99	0.983	0.958	0.947	0.938	0.923	0.912
<i>n</i>	7	8	9	9	9	9	9	9	8	8	8
$\text{M}^{3+}$ ion	Ho	Er	Tm	Yb	Lu	Pu	Ti	V	Cr	Fe	Co
Ionic radius (Å)	0.901	0.89	0.88	0.868	0.861	1.00	0.670	0.640	0.615	0.645	0.545
<i>n</i>	8	8	8	8	8	9	6	6	6	6	6

water to form *mer*-[ScCl<sub>3</sub>(THF)<sub>2</sub>(H<sub>2</sub>O)] (also octahedral), also for [Sc(Me<sub>3</sub>PO)<sub>6</sub>](NO<sub>3</sub>)<sub>3</sub>. Likewise, scandium is six coordinate in [Sc(dmsO)<sub>6</sub>](ClO<sub>4</sub>)<sub>3</sub> and also in [Sc(dmsO)<sub>6</sub>]I<sub>3</sub>, where X-ray diffraction on crystals and EXAFS studies on solutions yield similar Sc–O distances [2.069(3) Å and 2.09(1) Å, respectively]. However, [Sc(pu)<sub>6</sub>](O<sub>3</sub>SCF<sub>3</sub>)<sub>3</sub> (pu = tetrahydro-2-pyrimidone, a monodentate O-donor) has scandium in trigonal prismatic 6 coordination.

There are a number of  $\beta$ -diketonate complexes, like Sc(acac)<sub>3</sub>; this has octahedral 6 coordination [like M(acac)<sub>3</sub> for M = Ti–Co] and does not show any tendency to form adducts with Lewis bases, as do the lanthanide analogues. When nitrate is involved as a ligand, higher coordination numbers become possible, because a bidentate nitrate group takes up little more space in the coordination sphere than many monodentate ligands (has a small ‘bite angle’). Thus in the pentakis(nitrato)scandate ion in (NO<sup>+</sup>)<sub>2</sub>[Sc(NO<sub>3</sub>)<sub>5</sub>], nine coordination exists with one nitrate being monodentate. Eight coordination is found in Sc(Ph<sub>3</sub>PO)<sub>2</sub>( $\eta^2$ -NO<sub>3</sub>)<sub>3</sub> and [Sc(urea)<sub>4</sub>( $\eta^2$ -NO<sub>3</sub>)<sub>2</sub>]<sup>+</sup>(NO<sub>3</sub>)<sup>–</sup>. Similarly, Na<sub>5</sub>[Sc(CO<sub>3</sub>)<sub>4</sub>].2H<sub>2</sub>O features four bidentate carbonates surrounding scandium. Another way of obtaining high coordination numbers is to use multidentate ligands like EDTA. Crystals of NH<sub>4</sub>Sc(edta).5H<sub>2</sub>O contain [Sc(edta)(H<sub>2</sub>O)<sub>2</sub>]<sup>–</sup> ions, in which edta is (as usual) hexadentate and scandium is thus 8 coordinate (a case where X-ray diffraction studies are essential in determining how many water molecules are bound). Similarly, dtpa is octadentate in Mn[Sc(dtpa)].4H<sub>2</sub>O, so that scandium is 8 coordinate here too.

Lanthanide nitrate complexes of crown ethers have been studied in detail (Section 4.3.7). Scandium nitrate does not bind directly to crown ethers; complexes like Sc(NO<sub>3</sub>)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>.crown (crown = 15-crown-5, benzo-15-crown-5) do not involve direct bonds between the oxygens in the ether ring and scandium, instead they have hydrated scandium nitrate molecules linked to the crown ether by hydrogen bonds to the ether oxygens. However, reaction of ScCl<sub>3</sub> with halogen-extractor SbCl<sub>5</sub> and 15-crown-5 in acetonitrile gives [ScCl<sub>2</sub>(15-crown-5)](SbCl<sub>6</sub>) in which the scandium is bound to 5 ether oxygens and two chlorines in roughly pentagonal bipyramidal coordination. What has happened is that removal of a chlorine from ScCl<sub>3</sub> has effectively generated a linear ScCl<sub>2</sub> moiety that is ‘threaded’ through the crown ether ring. Similar reactions occur with some other crown ethers (benzo-15-crown-5, 18-crown-6; in the latter case the crown ether is only pentadentate – see Figure 7.2). Carrying out the reaction in THF in the absence of crown ether gives [ScCl<sub>2</sub>(THF)<sub>4</sub>]<sup>+</sup>[SbCl<sub>5</sub>(THF)]<sup>–</sup>; in contrast, Y and La form [LnCl<sub>2</sub>(THF)<sub>5</sub>]<sup>+</sup>[SbCl<sub>5</sub>(THF)]<sup>–</sup>.



**Figure 7.2**

Seven-coordinate scandium in [ScCl<sub>2</sub>(18-crown-6)](SbCl<sub>6</sub>) (reproduced by permission of the Royal Society of Chemistry from G.R. Willey, M.T. Lakin, and N.W. Alcock, *J. Chem. Soc., Chem. Commun.*, 1992, 1619).

$\text{Sc}(\text{THF})_3\text{Cl}_3$  is a very useful synthon (starting material) for other scandium compounds. It can conveniently be prepared using thionyl dichloride as a dehydrating agent:

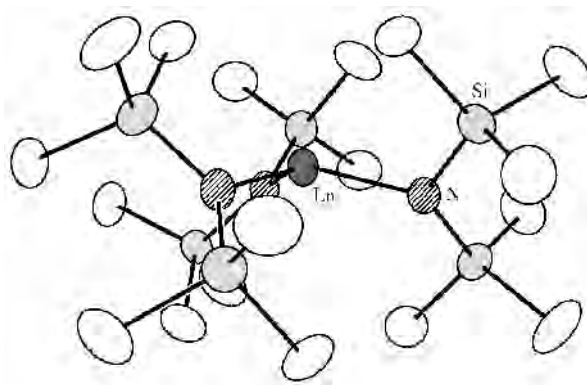


Ammine complexes cannot be made by solution methods, as owing to the basicity of ammonia other species (possibly hydroxy complexes) are obtained, but a few ammines have recently been described.  $(\text{NH}_4)_2[\text{Sc}(\text{NH}_3)_5\text{I}]$  is obtained as pink crystals from the reaction of  $\text{NH}_4\text{I}$  and metallic scandium in a sealed tube at  $500^\circ\text{C}$ . Sc reacts with  $\text{NH}_4\text{Br}$  on heating in a sealed tantalum container, forming  $[\text{Sc}(\text{NH}_3)_2\text{Br}_3]$ , isotypic with  $\text{Sc}(\text{NH}_3)_2\text{Cl}_3$ , which has the structure  $[\text{Sc}_2\text{Br}_6(\text{NH}_3)_4]$ , with isolated dimers of bromide edge-connected  $[\text{Sc-mer}-(\text{NH}_3)_3\text{Br}_3]$  and  $[\text{Sc}(\text{NH}_3)\text{Br}_5]$  octahedra.  $[\text{Sc}(\text{NH}_3)\text{Br}_3]$ , isotypic with  $\text{Sc}(\text{NH}_3)\text{Cl}_3$ , is  $[\text{Sc}_2\text{Br}_6(\text{NH}_3)_2]$ , with zigzag chains of edge-connected  $[\text{Sc}(\text{NH}_3)\text{Br}_5]$  octahedra as  $[\text{Sc}(\text{NH}_3)_{1/1}\text{Br}_{1/1}\text{Br}_{4/2}]$ . Scandium similarly reacts with  $\text{NH}_4\text{Cl}$  in the presence of  $\text{CuCl}_2$  to form  $[\text{ScCl}_3(\text{NH}_3)]$  and  $[\text{ScCl}_3(\text{NH}_3)_2]$ . Scandium has octahedral coordination in all of these.

### 7.3.3 Alkoxides and Alkylamides

Scandium resembles the 3d transition metals from titanium through cobalt in forming an unusual three-coordinate silylamide  $\text{Sc}[\text{N}(\text{SiMe}_3)_2]_3$  but unlike them its solid-state structure is pyramidal (Figure 7.3), not planar, in which respect it resembles the lanthanides and uranium. It does not form adducts with Lewis bases, presumably on steric grounds, the resemblance here being to the 3d metals. However, the compound of a less congested amide ligand forms  $[\text{Sc}\{\text{N}(\text{SiHMe}_2)_2\}_3(\text{THF})]$ , which has distorted tetrahedral four coordination of scandium, with short Sc.....Si contacts in the solid state; this is in contrast to the 5-coordinate  $[\text{Ln}\{\text{N}(\text{SiHMe}_2)_2\}_3(\text{THF})_2]$ .

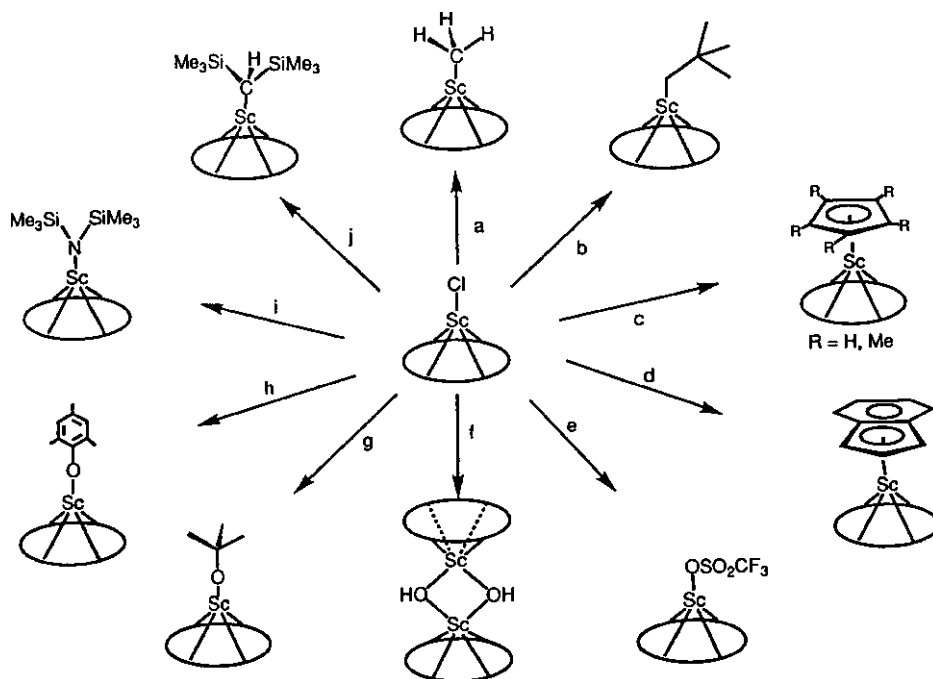
Few scandium alkoxides have been studied in detail, but monomeric 3-coordination exists in  $[(2,6\text{-Bu}'_2\text{-4-MeC}_6\text{H}_2\text{O})_3\text{Sc}]$  where the bulky ligand enforces steric crowding. It will, however, expand its coordination sphere to form 4-coordinate adducts with  $\text{Ph}_3\text{PO}$  and THF – unlike the corresponding three-coordinate silylamide.  $\text{Sc}(\text{OSiBu}'_3)_3 \cdot \text{L}$  ( $\text{L} = \text{THF}$ ,



**Figure 7.3**

Three-coordinate  $\text{Sc}[\text{N}(\text{SiMe}_3)_2]_3$  (where  $\text{Ln} = \text{Sc}$ ) (reproduced by permission of the Royal Society of Chemistry from J.S. Ghotra, M.B. Hursthouse, and A.J. Welch, *J. Chem. Soc., Chem. Commun.*, 1973, 669).

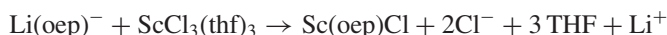


**Figure 7.4**

Conditions: (a)  $\text{Me}_2\text{Mg}$  in toluene; (b)  $\text{Np}_2\text{Mg}$  in toluene; (c)  $\text{NaCp}$  in THF,  $\text{LiCp}^*$  in THF,  $\text{Li}(\text{MeCp})$  in THF; (d)  $\text{Na}(\text{Ind})$  in THF; (e)  $\text{TMSOTf}$  in toluene; (f)  $\text{H}_2\text{O}$  in  $\text{CH}_2\text{Cl}_2$ ; (g)  $\text{LiOCMe}_3$  in toluene; (h)  $\text{LiO}(\text{Me}_3\text{C}_6\text{H}_2)$  in toluene; (i)  $\text{NaN}(\text{TMS})_2$  in toluene; (j)  $\text{LiCH}(\text{SiMe}_3)_2$  in toluene (reproduced with permission from J. Arnold *et al.*, *Organometallics*, 1993, **12**, 3646 © American Chemical Society 2005).

py,  $\text{NH}_3$ ) have also been prepared (the Lewis base cannot, however, be removed to afford the homoleptic siloxide).

Relatively few complexes of N-donor ligands are known. One of the best characterized is with the tridentate ligand terpyridyl, which reacts with scandium nitrate to form  $\text{Sc}(\text{terpy})(\text{NO}_3)_3$ ; here scandium is connected to 9 atoms, but one Sc–O bond is considerably longer than the others, so a coordination number of 8.5 has been assigned. A range of porphyrin and phthalocyanine complexes exist; syntheses often involve the high-temperature routes typical of the transition metals but recently a high-yield low-temperature route has been utilized to make octaethylporphyrin (OEP) complexes:



The chloride can be replaced by alkoxy, alkylamide, alkyl, and cyclopentadienyl groups, as shown in Figure 7.4.

### 7.3.4 Patterns in Coordination Number

Table 7.3 lists in parallel corresponding binary compounds and complexes of scandium, lanthanum, and lutetium. As expected on steric grounds, the smaller scandium generally

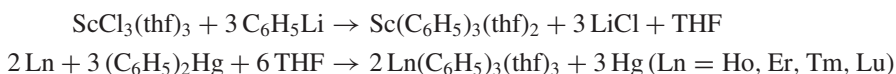
Table 7.3

Compound	Sc compound/complex		La compound/complex		Lu compound/complex	
	Formula	C.N.	Formula	C.N.	Formula	C.N.
Oxide	Sc <sub>2</sub> O <sub>3</sub>	6	La <sub>2</sub> O <sub>3</sub>	7	Lu <sub>2</sub> O <sub>3</sub>	6
Fluoride	ScF <sub>3</sub>	6	LaF <sub>3</sub>	9+2	LuF <sub>3</sub>	9
Chloride	ScCl <sub>3</sub>	6	LaCl <sub>3</sub>	9	LuCl <sub>3</sub>	6
Bromide	ScBr <sub>3</sub>	6	LaBr <sub>3</sub>	9	LuBr <sub>3</sub>	6
Iodide	ScI <sub>3</sub>	6	LaI <sub>3</sub>	8	LuI <sub>3</sub>	6
Acetylacetonate	Sc(acac) <sub>3</sub>	6	La(acac) <sub>3</sub> (H <sub>2</sub> O) <sub>2</sub>	8	Lu(acac) <sub>3</sub> (H <sub>2</sub> O)	7
EDTA complex	Sc(EDTA)(H <sub>2</sub> O) <sub>2</sub> <sup>-</sup>	8	La(EDTA)(H <sub>2</sub> O) <sub>3</sub> <sup>-</sup>	9	Lu(EDTA)(H <sub>2</sub> O) <sub>2</sub> <sup>-</sup>	8
THF adduct of trichloride	ScCl <sub>3</sub> (THF) <sub>3</sub>	6	[LaCl(μ-Cl) <sub>2</sub> (THF) <sub>2</sub> ] <sub>n</sub>	8	LuCl <sub>3</sub> (THF) <sub>3</sub>	6
Terpy complex of nitrate	Sc(NO <sub>3</sub> ) <sub>3</sub> (terpy)	8.5	La(NO <sub>3</sub> ) <sub>3</sub> (terpy)(H <sub>2</sub> O) <sub>2</sub>	11	Lu(NO <sub>3</sub> ) <sub>3</sub> (terpy)	9
Aqua ion	[Sc(H <sub>2</sub> O) <sub>7</sub> ] <sup>3+</sup>	7	[La(H <sub>2</sub> O) <sub>9</sub> ] <sup>3+</sup>	9	[Lu(H <sub>2</sub> O) <sub>8</sub> ] <sup>3+</sup>	8
Bis(trimethylsilyl)amide	Sc{N(SiMe <sub>3</sub> ) <sub>2</sub> } <sub>3</sub>	3	La{N(SiMe <sub>3</sub> ) <sub>2</sub> } <sub>3</sub>	3	Lu{N(SiMe <sub>3</sub> ) <sub>2</sub> } <sub>3</sub>	3
Ph <sub>3</sub> PO complex of nitrate	Sc(η <sup>2</sup> -NO <sub>3</sub> ) <sub>3</sub> (Ph <sub>3</sub> PO) <sub>2</sub>	8	La(η <sup>1</sup> -NO <sub>3</sub> )(η <sup>2</sup> -NO <sub>3</sub> ) <sub>2</sub> (Ph <sub>3</sub> PO) <sub>4</sub>	9	[Lu(η <sup>2</sup> -NO <sub>3</sub> ) <sub>2</sub> (Ph <sub>3</sub> PO) <sub>4</sub> ]NO <sub>3</sub>	8

exhibits lower coordination numbers than the lanthanides, although sometimes the value is the same as for lutetium, the smallest lanthanide.

## 7.4 Organometallic Compounds of Scandium

The organometallic chemistry of scandium is generally similar to that of the later lanthanides. It thus forms a cyclopentadienyl  $\text{ScCp}_3$  that has mixed mono- and pentahapto-coordination like  $\text{LuCp}_3$ . An anionic methyl  $[\text{Li}(\text{tmed})]_3[\text{M}(\text{CH}_3)_6]$  is formed by scandium, as by the lanthanides. However, there are often subtle differences that should be borne in mind. The pentamethylcyclopentadienyl compound  $[\text{ScCp}^*_2\text{Me}]$  is a monomer but the lutetium compound is an asymmetric dimer  $[\text{Cp}^*_2\text{Lu}(\mu\text{-Me})\text{LuCp}^*_2\text{Me}]$ . Similarly, whilst triphenylscandium is obtained as a bis(thf) adduct,  $[\text{ScPh}_3(\text{thf})_2]$ , which has a TBPY structure with axial thf molecules, the later lanthanides form octahedral  $[\text{LnPh}_3(\text{thf})_3]$ . Triphenylscandium and the phenyls of the later lanthanides are made by different routes.



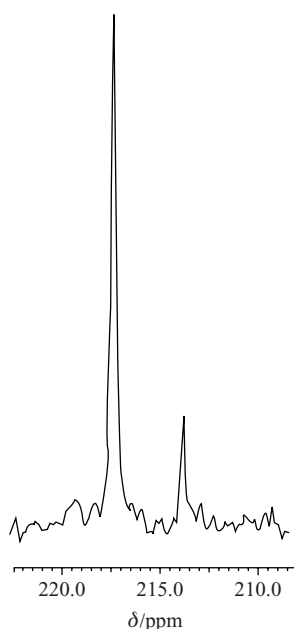
Thus, the synthesis of triphenylscandium is a salt-elimination reaction (or metathesis) whilst the route for the lanthanide phenyls involves a redox reaction. The former has the problem of producing LiCl, which is often significantly soluble in organic solvents and contaminates the desired product, whilst the latter involves disposal of mercury waste, as well as handling toxic organomercury compounds.

## 7.5 Yttrium

As discussed earlier, yttrium resembles the later lanthanides strongly in its chemistry, so that throughout this book, discussion of lanthanide chemistry includes yttrium, and its compounds will not be examined in this chapter. To give a few, almost random, examples of yttrium compounds strongly resembling those of the later lanthanides:

- $\text{YX}_3$  ( $\text{X} = \text{F, Cl, Br, I}$ ) have the same structures as  $\text{LnX}_3$  ( $\text{Ln} = \text{Dy-Lu}$ );
- the yttrium aqua ion is  $[\text{Y}(\text{H}_2\text{O})_8]^{3+}$  though solid yttrium triflate  $\text{Y}(\text{O}_3\text{SCF}_3)_3 \cdot 9\text{H}_2\text{O}$  contains  $[\text{Y}(\text{H}_2\text{O})_9]^{3+}$  ions;
- the acetylacetonate is  $[\text{Y}(\text{acac})_3(\text{H}_2\text{O})]$ ;
- the bis(trimethylsilyl)amide is  $\text{Y}[\text{N}(\text{SiMe}_3)_2]_3$ ;
- terpyridyl reacts with yttrium nitrate, forming 10 coordinate  $[\text{Y}(\text{terpy})(\text{NO}_3)_3(\text{H}_2\text{O})]$ .

Yttrium compounds are frequently useful host materials for later  $\text{Ln}^{3+}$  ions, as mentioned in Section 5.4.4;  $\text{Eu:Y}_2\text{O}_2\text{S}$  is the standard material for the red phosphor in virtually all colour and television cathode ray tubes, whilst  $\text{Eu:Y}_2\text{O}_3$  is used for energy-efficient fluorescent tubes. Yttrium oxide is used to stabilize zirconia (YSZ), yttrium iron garnets (YIG) are used in microwave devices, and of course  $\text{YBa}_2\text{Cu}_3\text{O}_7$  is the classic ‘warm’ superconductor. Yttrium, like scandium, is naturally monoisotopic.  $^{89}\text{Y}$  has  $I = 1/2$ ; though signals can be difficult to observe, valuable information can be obtained from NMR studies.



**Figure 7.5**

$^{89}\text{Y}$  NMR spectrum of  $[\text{Y}_5\text{O}(\text{O}^i\text{Pr})_{13}]$  in  $\text{C}_6\text{D}_6$  at  $25^\circ\text{C}$  (reproduced with permission of the American Chemical Society from P.S Coan, L.G. Hubert-Pjälzgraf, and H.G. Caulton, *Inorg. Chem.*, 1992, **31**, 1262).

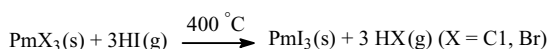
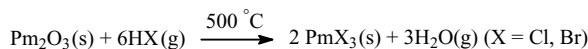
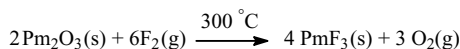
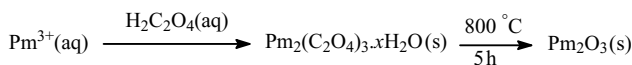
Reaction of  $\text{YCl}_3$  with lithium isopropoxide,  $\text{LiOCHMe}_2$  ( $\text{LiOPr}^i$ ), affords an alkoxide  $\text{Y}_5\text{O}(\text{OPr}^i)_{13}$ , which does not have a simple structure but has a cluster of 5 yttriums arranged round a central oxygen. The  $^{89}\text{Y}$  NMR spectrum is shown in Figure 7.5.

Two possible geometries, square pyramidal and trigonal bipyramidal, are possible for the  $\text{Y}_5\text{O}$  core of the molecule; the two NMR signals have relative intensities of 4:1, supporting the square pyramidal structure. Use of bulky R groups, such as  $\text{OCBu}_3^t$  or  $2,6\text{-Bu}_2\text{C}_6\text{H}_3$ , would mean that a monomeric  $\text{Y}(\text{OR})_3$  system is more likely.

## 7.6 Promethium

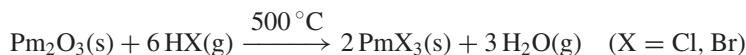
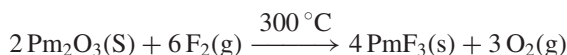
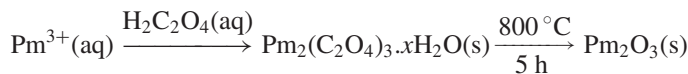
Mendeleev's Periodic Table made no provision for a lanthanide series. No one could predict how many of these elements would exist and it was not until Moseley's work on X-ray spectra that resulted in the concept of atomic number (1913) that it was known that an element with atomic number 61, situated between neodymium and samarium, remained to be discovered. Although several claims were made for its discovery in lanthanide ores, it was realized that no stable isotopes of element 61 existed and, from the late 1930s, nuclear chemistry was applied to its synthesis.

Promethium occurs in tiny amounts in uranium ores, thus a sample of Congolese pitchblende was found to contain  $(4 \pm 1) \times 10^{-15}\text{g}$  of  $^{147}\text{Pm}$  per kg of ore; it was formed mainly by spontaneous fission of  $^{238}\text{U}$ . It is also one of the fission products of uranium-235 and can be obtained from a mixture of lanthanides by ion exchange. The longest-lived isotope is

**Figure 7.6**

Syntheses of  $\text{Pm}_2\text{O}_3$ ,  $\text{PmF}_3$ ,  $\text{PmCl}_3$ ,  $\text{PmBr}_3$ , and  $\text{PmI}_3$ .

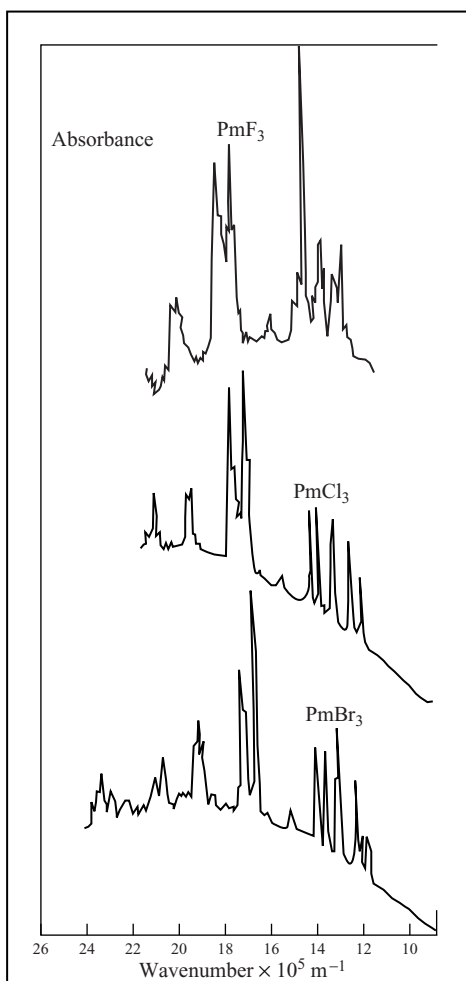
$^{145}\text{Pm}$  ( $t_{1/2} = 17.7$  y) although a number of other isotopes exist, with both  $^{146}\text{Pm}$  ( $t_{1/2} = 5.5$  y) and  $^{147}\text{Pm}$  ( $t_{1/2} = 2.62$  y) also having quite long half-lives. Because of its radioactivity and also because it is only available in relatively small amounts, chemical studies are difficult and relatively rare. A study of the oxide and halides began with about 100  $\mu\text{g}$  of the oxide  $\text{Pm}_2\text{O}_3$ . Starting from this, all the halides were synthesized microchemically, carrying out the reactions in quartz capillaries (Figure 7.6).



On account of the small amounts available, the compounds were characterized by non-destructive techniques – X-ray powder diffraction, Raman spectroscopy, and UV–visible spectra. Purple-pink  $\text{PmF}_3$  (mp 1338  $^\circ\text{C}$ ) has the 11-coordinate  $\text{LaF}_3$  structure, lavender  $\text{PmCl}_3$  (mp 655  $^\circ\text{C}$ ) has the 9-coordinate  $\text{UCl}_3$  structure, and coral-red  $\text{PmBr}_3$  (mp 624  $^\circ\text{C}$ ) has the 8-coordinate  $\text{PuBr}_3$  structure. Red  $\text{PmI}_3$  (mp 695  $^\circ\text{C}$ ) has the eight-coordinate  $\text{PuBr}_3$  structure at room temperature but the six-coordinate  $\text{BiI}_3$  structure at high temperatures.  $\text{Pm}_2\text{O}_3$  itself can crystallize in one of three modifications; in the case in question, it was obtained in the B-type structure also adopted by the Sm, Eu, and Gd oxides.

Figure 7.7 shows the UV–visible absorption spectra of three promethium halides measured at room temperature. These very sharp absorption bands are characteristic of a lanthanide; if they came from a transition metal, they would be much broader. They also show very little dependence upon halide, showing that ligand-field effects are almost negligible; the position of the maxima would vary much more if promethium were a transition metal. (Although this is not shown in the diagram, the extinction coefficients are also much lower than for a transition metal.)

Other promethium compounds that have been isolated include the hydroxide  $\text{Pm}(\text{OH})_3$  [which adopts the 9-coordinate structure of  $\text{Nd}(\text{OH})_3$ ] and hydrated salts including



**Figure 7.7**

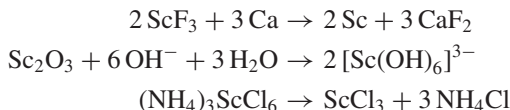
Solid-state absorption spectra of  $\text{PmF}_3$ ,  $\text{PmCl}_3$ , and  $\text{PmBr}_3$  (reproduced with permission from W.K. Wilmarth *et al.*, *J. Less Common Metals*, 1988, **141**, 275).

$\text{PmCl}_3 \cdot x\text{H}_2\text{O}$ ,  $\text{Pm}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ , and  $\text{Pm}(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$ . It would be expected that promethium would form some stable compounds in the +2 oxidation state, though they are unlikely to be made in aqueous solution. No definite evidence has yet been obtained, since studies have been hindered both by the small quantities of the element available and by its radioactivity. The properties of promethium fit neatly into position between neodymium and samarium; it is a microcosm of lanthanide chemistry in general.

**Question 7.1** (a) Write equations for the (i) reduction of  $\text{ScF}_3$  by calcium, (ii) scandium oxide dissolving in potassium hydroxide solution, (iii) the thermal decomposition of  $(\text{NH}_4)_3\text{ScCl}_6$ . (b) Why is the thermal decomposition of  $(\text{NH}_4)_3\text{ScCl}_6$  a good way of making pure  $\text{ScCl}_3$ ?

**Answer (7.1)**

(a)



(b) No water is present that could cause hydrolysis and the other product of the reaction, ammonium chloride, sublimates on gentle heating, giving a pure product.

**Question 7.2**  $\text{MgCl}_2$  melts at 712 °C and boils at 1712 °C;  $\text{ScCl}_3$  normally sublimates at 800 °C;  $\text{AlCl}_3$  sublimates at 178 °C. Account for these results in terms of the covalent character in the bonding.

**Answer 7.2**  $\text{MgCl}_2$  has a substantially ionic structure, giving it the highest electrostatic forces, and hence the highest melting point.  $\text{ScCl}_3$  and, even more,  $\text{AlCl}_3$  have increasing covalent contributions to the bonding ( $\text{AlCl}_3$  sublimates as  $\text{Al}_2\text{Cl}_6$  units) so that the attractive forces between the (smaller) molecular units increase. Fajans' rules predict that covalent character increases with (1) decrease in ionic size (aluminium is smaller than scandium) and (2) increasing charge on the ion.

**Question 7.3**  $\text{ScH}_2$  conducts electricity well. Suggest a reason.

**Answer 7.3** It is probably a scandium(III) compound  $\text{Sc}^{3+}(\text{H}^-)_2(\text{e}^-)$ . The free electrons are in a delocalized conduction band and thus enable it to conduct electricity.

**Question 7.4** Predict coordination numbers for (a)  $\text{Rb}_2\text{KScF}_6$ ; (b)  $\text{Ba}_2\text{ScCl}_7$ ; (c)  $[\text{ScCl}_3\{\text{MeO}(\text{CH}_2)_2\text{OMe}\}(\text{MeCN})]$ ; (d)  $\text{Sc}(\text{Ph}_2\text{MePO})_4(\text{NO}_3)_3$ ; (e)  $\text{ScX}_3(\text{Ph}_3\text{PO})_4$  ( $\text{X} = \text{Cl}, \text{Br}$ ).

**Answer 7.4** (a) 6, contains  $[\text{ScF}_6]^{3-}$  ions; (b) 6, has structure  $\text{Ba}_2[\text{ScCl}_6]\text{Cl}$  – possibly not predictable; (c) 6,  $\text{MeO}(\text{CH}_2)_2\text{OMe}$  is bidentate and  $\text{MeCN}$  is N-bonded; (d) 8,  $[\text{Sc}(\text{Ph}_2\text{MePO})_4(\eta^2\text{-NO}_3)_2]^+(\text{NO}_3)^-$ ; a monomeric  $\text{Sc}(\text{Ph}_2\text{MePO})_4(\eta^2\text{-NO}_3)_3$  would be 10 coordinate; (e) 6,  $[\text{ScX}_2(\text{Ph}_3\text{PO})_4]\text{X}$  ( $\text{X} = \text{Cl}, \text{Br}$ ).

**Question 7.5** Why are yttrium compounds good host materials for heavier  $\text{Ln}^{3+}$  ions?

**Answer 7.5** Because  $\text{Y}^{3+}$  has no f (or d electrons), its compounds have no absorptions in the visible region of the spectrum and do not affect the magnetic properties of any added lanthanide ions. Because its ionic radius is similar to that of  $\text{Ho}^{3+}$ , it can accommodate several of the later lanthanide ions with minimal distortion.

**Question 7.6** Suggest why the synthetic routes and spectroscopic methods shown for the binary promethium compounds in Section 7.6 were employed.

**Answer 7.6** Only one product is a solid; by-products are gases and thus easily separated without loss of the desired product (important with small quantities). The products in the capillaries can then conveniently be used for X-ray diffraction studies (and UV–visible and Raman spectroscopy).

**Question 7.7** Why are the structures of promethium compounds determined by powder methods and not by single-crystal methods?

**Answer 7.7** The radiation emitted rapidly destroys the regular lattice in a single crystal.

**Question 7.8** The visible spectrum of a promethium(III) compound (Figure 7.7) contains a considerable number of bands. How could you show that none of these were caused by impurity?

**Answer 7.8** Wait for a few years (!), then remeasure the spectrum, any bands due to decay products will have become stronger and genuine bands due to  $\text{Pm}^{3+}$  will have diminished. Next, purify the promethium by ion exchange, then reprepare the compound; the impurity bands should have vanished.

**Question 7.9** Explain why it is unlikely that  $\text{Pm}^{2+}$  compounds could be prepared by reduction in aqueous solution. (Hint: consult the reduction potentials in Table 2.7). Assuming that this were possible, why would  $\text{PmSO}_4$  be a good choice of compound to isolate? Suggest a solvent that might be a good choice.

**Answer 7.9** The reduction potential of  $\text{Pm}^{2+}(\text{Pm}^{3+}/\text{Pm}^{2+} = -2.6 \text{ V})$  is such that it is likely to be a very good reducing agent and would react with water.  $\text{PmSO}_4$  is expected by analogy with  $\text{EuSO}_4$  to be very insoluble and therefore could be followed by tracer study. A coordinating but non-aqueous solvent like THF would be a good choice.





# 8 The Lanthanides and Scandium in Organic Chemistry

By the end of this chapter you should be able to:

- recognize key lanthanide compounds used in organic reactions;
- appreciate some of the reactions in which they can be used;
- suggest reagents for certain transformations.

## 8.1 Introduction

It is a commonplace to say that there has been explosive growth in the use of lanthanides in organic chemistry. For many years, the use of cerium(IV) compounds as oxidants was widespread, but more recently a whole range of other compounds have made their appearance. Thus samarium(II) compounds are now routinely used as one-electron reducing agents and the use of trifluoromethanesulfonate ('triflate') salts of scandium and the lanthanides as water-soluble Lewis acid catalysts is widespread. Beta-diketonate complexes and alkoxides have also come into use; there are even applications of mischmetal in organic synthesis.

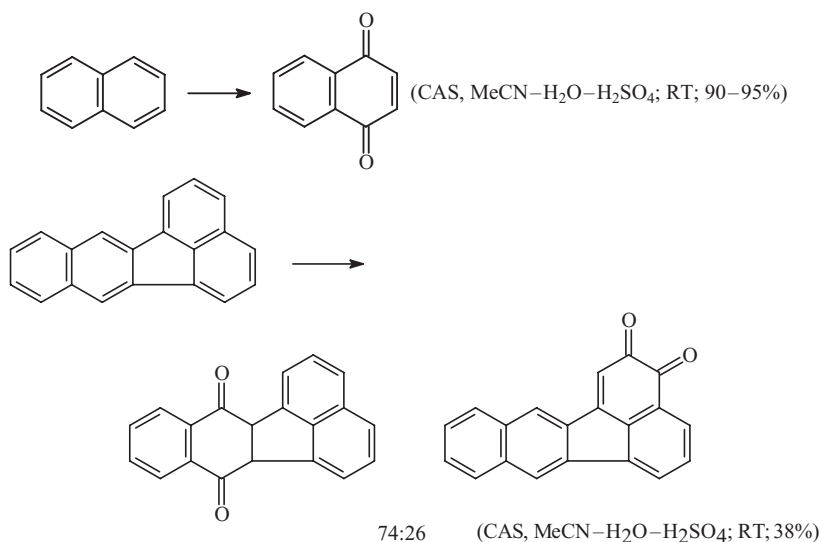
## 8.2 Cerium(IV) Compounds

Cerium is the most stable lanthanide in the (+4) oxidation state, so  $\text{Ce}^{\text{IV}}$  compounds have long been used as oxidants, most often as the nitrate complex,  $(\text{NH}_4)_2[\text{Ce}(\text{NO}_3)_6]$  [cerium(IV) ammonium nitrate; CAN], but also  $(\text{NH}_4)_4[\text{Ce}(\text{SO}_4)_4]$  [cerium(IV) ammonium sulphate; CAS] in particular, along with cerium trifluoroacetate and others. The redox potential depends on the medium; in aqueous solution it is pH sensitive, getting more positive (i.e., more strongly oxidizing) the more acidic the solution. Mixtures of cerium salts with sodium bromate have been used, since the bromate is an oxidizing agent that can regenerate the  $\text{Ce}^{\text{IV}}$  state, permitting the use of cerium in catalytic, rather than stoichiometric, quantities.

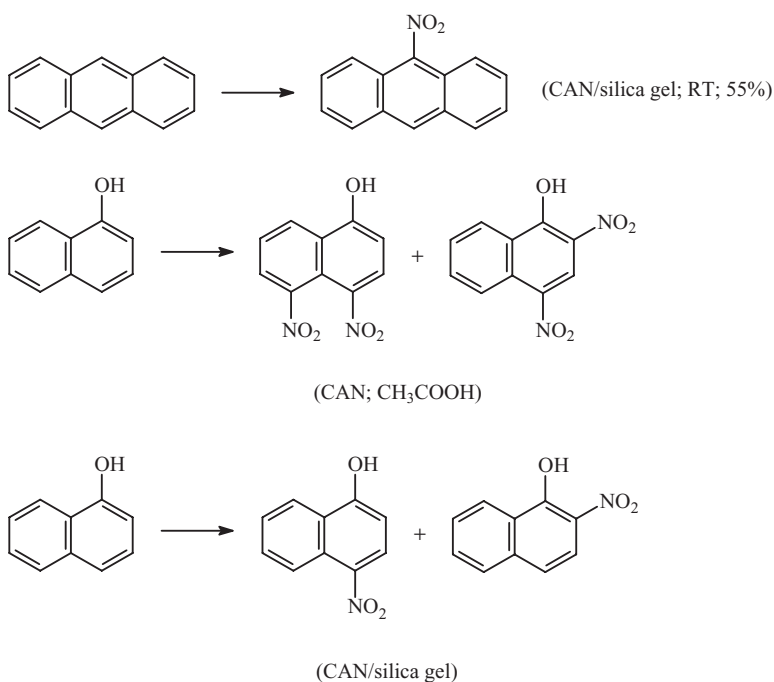
### 8.2.1 Oxidation of Aromatics

When working in acidic solution, arenes are generally oxidized to quinones; reasonable yields are obtained with symmetric hydrocarbons as starting molecules, but

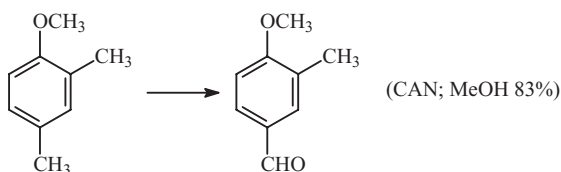
non-symmetrical arenes lead to several products. CAS is the reagent of choice for these oxidations, as use of CAN may lead to introduction of nitro groups into the aromatic rings.



Working in other media, the rings can be functionalized instead of being converted into quinones.



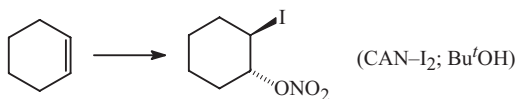
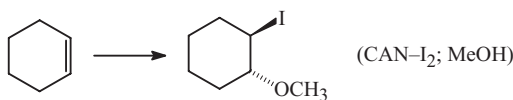
Ce<sup>IV</sup> Compounds oxidize side chains of aromatic compounds effectively and selectively, methylene carbons at the benzylic positions being oxidized to carbonyl groups. Polymethylated aromatics generally are oxidized to a single aldehyde group.



If alkylbenzenes are oxidized in non-aqueous media, other products are obtained; working in ethanoic acid, acetates are formed; in alcohol, ethers result.

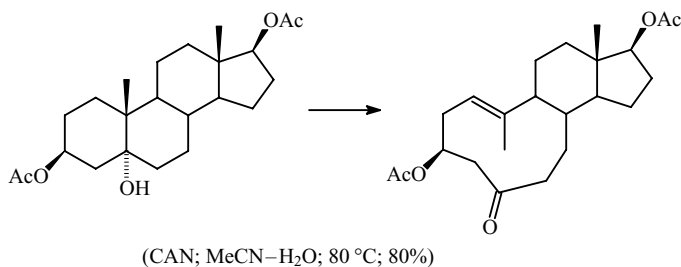
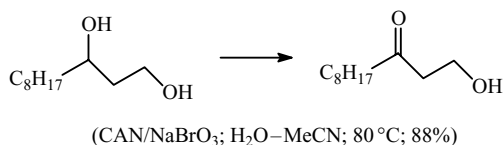
### 8.2.2 Oxidation of Alkenes

Alkenes are readily oxidized, products depending strongly upon the solvent and also upon nucleophiles present.



### 8.2.3 Oxidation of Alcohols

There are a variety of products, depending upon the alcohol. Allylic and benzylic alcohols are easily oxidized under mild conditions. Secondary alcohols are oxidized under rather stronger conditions. Simple primary alcohols (i.e., not 'activated' benzylic alcohols) are not oxidized. The oxidation of tertiary alcohols is accomplished with C–C bond fission.

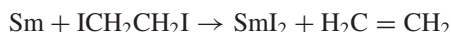


The last named is an example of a Grob oxidative fragmentation.

### 8.3 Samarium(II) Iodide, SmI<sub>2</sub>

This is a powerful but selective 1-electron reducing agent, whose use was pioneered especially by Henri B. Kagan. Soluble in solvents such as alcohols and THF, its activity can be improved by adding a strong donor ligand, typically a Lewis base such as hexamethylphosphoramide [HMPA; (Me<sub>2</sub>N)<sub>3</sub>PO]. Reaction proceeds at an optimum HMPA: Sm ratio of 4:1, the acceleration probably involving a complex like SmI<sub>2</sub>(hmpa)<sub>4</sub> (which has been isolated). Many reactions may involve radical intermediates.

A convenient synthesis is:



Carried out in THF at room temperature, this affords a deep blue solution. The effectiveness of SmI<sub>2</sub> for some reactions can also be enhanced with certain catalysts. Thus, nickel halides, especially NiI<sub>2</sub>, accelerate many reactions in THF, whilst iron(III) salts are used in samarium-assisted Barbier reactions. The choice of solvent is sometimes important; thus water or alcohols are sometimes added to accelerate reactions. A disadvantage is that large, stoichiometric, amounts of SmI<sub>2</sub> are needed, in fairly dilute mixtures, making its use costly, not least as large volumes of solvent are consumed; interest has developed in catalytic reactions, for example in the use of Mischmetal as a co-reducing agent for *in-situ* regeneration of SmI<sub>2</sub>.

#### 8.3.1 Reduction of Halogen Compounds

Halogen compounds are readily reduced, converting RX into alkanes in good yields. The reactivity order is I > Br > Cl. The process is very solvent-dependent; in THF only primary halides are reduced, but in HMPA primary, secondary, tertiary, and aryl halides are all reduced.

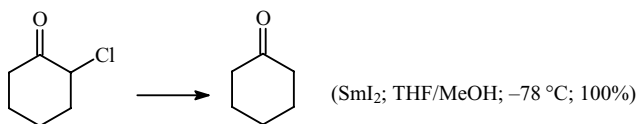


Sometimes coupling occurs:



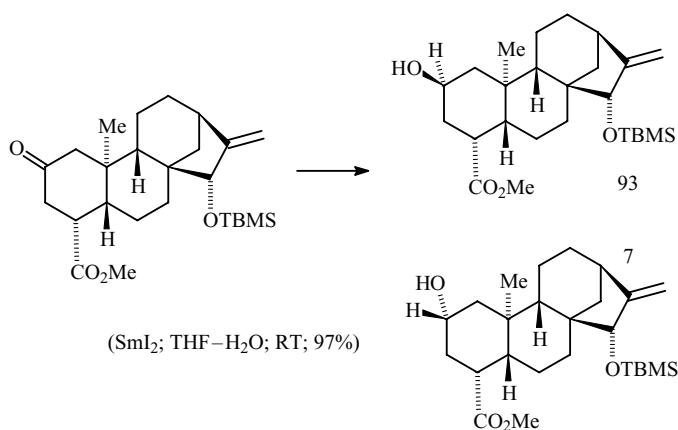
#### 8.3.2 Reduction of $\alpha$ -Heterosubstituted Ketones

This affords unsubstituted ketones



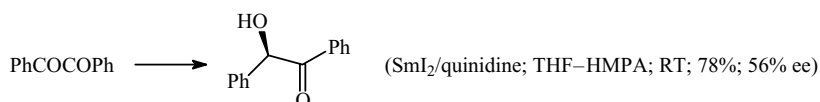
#### 8.3.3 Reductions of Carbonyl Groups

Two outcomes are possible. In the presence of a proton source (e.g., H<sub>2</sub>O) they are reduced to alcohols, as in E.J. Corey's approach to the synthesis of atracytogenin

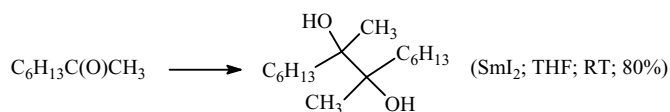


In this synthesis, the reactant was chosen to control stereochemistry and give an equatorial alcohol, due to an intermediate axial radical; use of hydride-transfer reagents would tend to afford predominantly the axial alcohol.

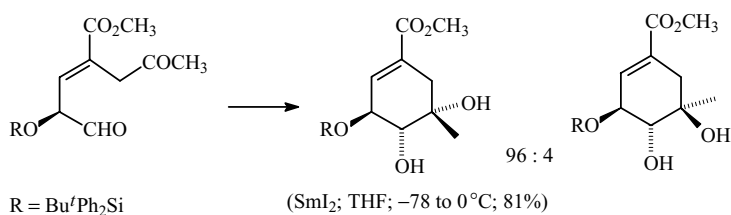
Asymmetric reduction of the carbonyl group occurs in the presence of a chiral base.



In the absence of a proton source, coupling to give pinacols occurs:

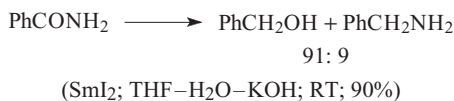
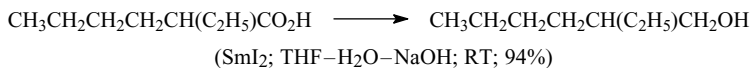


This can be used to create cyclic systems containing *cis*-vicinal diol units.



Carboxylic acids and esters (and other acid derivatives) are generally inert to  $\text{SmI}_2$ . However, in strongly basic or acidic conditions, reduction occurs: Carboxylic acids and amides are reduced to primary alcohols (amides afford some amine as secondary

product)

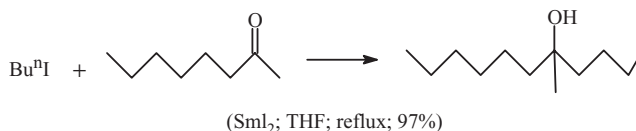


Nitriles are also reduced to amines



### 8.3.4 Barbier Reactions

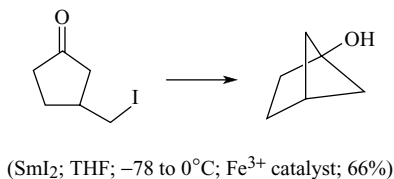
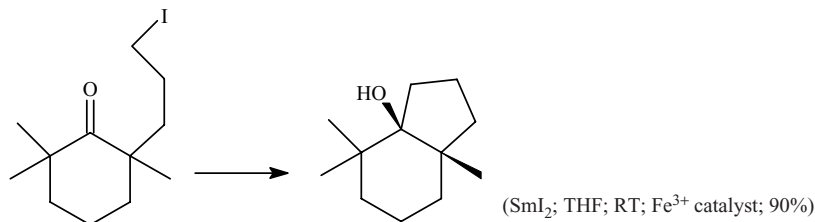
These involve addition of a halogenoalkane to a carbonyl compound.



This reaction can be carried out rapidly at room temperature by using small amounts of Fe<sup>3+</sup> catalyst. Considerable acceleration can be achieved by using hexamethylphosphoramide as a reaction medium (compare the following two reactions).

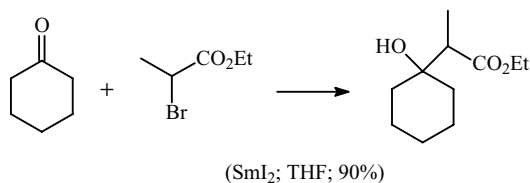


Intramolecular Barbier-type reactions occur between carbonyl and halogen groups in the same molecule:



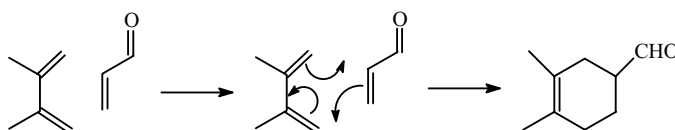
### 8.3.5 Reformatsky Reactions

These occur between  $\alpha$ -bromo esters and carbonyl compounds and are often used in ring-formation reactions.

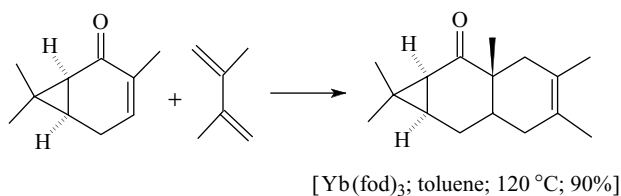
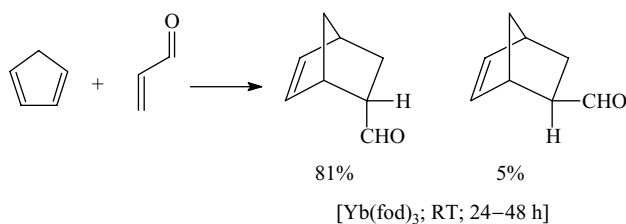


## 8.4 Lanthanide $\beta$ -Diketonates as Diels–Alder Catalysts

In the Diels–Alder reaction a diene (which must be capable of being *s-cis*) reacts with a dienophile, which must have an electron-withdrawing group conjugated to an alkene.



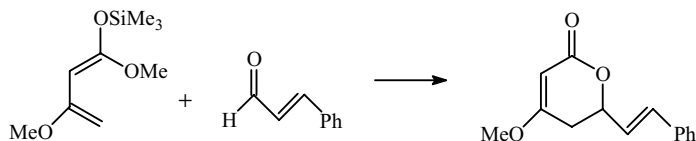
Lanthanide  $\beta$ -diketonate complexes,  $\text{Ln}(\text{fod})_3$ , widely used formerly as NMR shift reagents (Section 5.5.1) are employed ( $\text{fod} = 6,6,7,7,8,8,8\text{-heptafluoro-2,2-dimethyloctane-3,5-dionato}$ ). They have the advantages of working well under mild conditions (so that acid-sensitive groups are unaffected), as well as displaying good regio- and stereo-selectivity, with *endo*-adducts usually obtained.



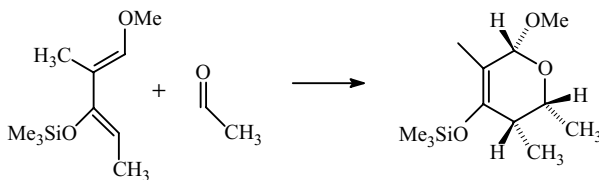


### 8.4.1 Hetero-Diels–Alder Reactions

Electron-rich alkenes, like the diene referred to in the first example, are very acid labile, so need a gentle catalyst. Aldehydes are the most usual dienophiles used in these syntheses.



[Eu(fod)<sub>3</sub>; CH<sub>2</sub>Cl<sub>2</sub>; RT, 48h; 84%]



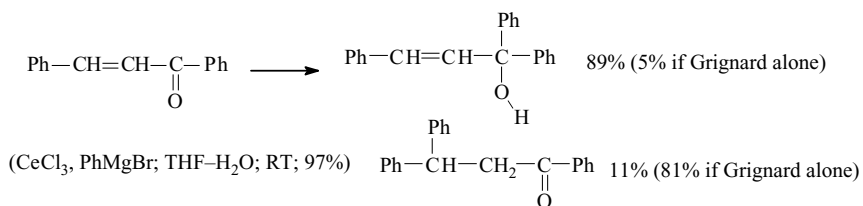
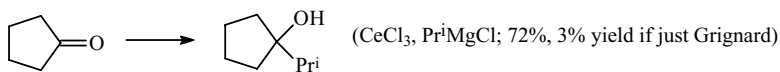
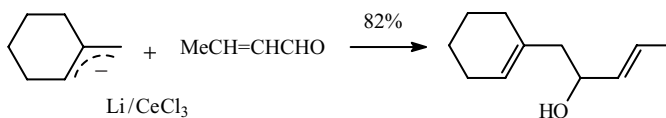
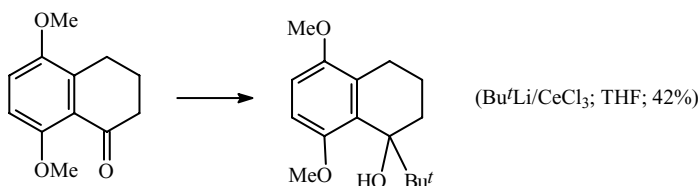
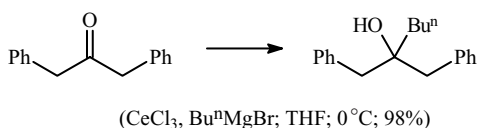
[Eu(fod)<sub>3</sub>; CHCl<sub>3</sub>; RT, 66%]

## 8.5 Cerium(III) Chloride and Organocerium Compounds

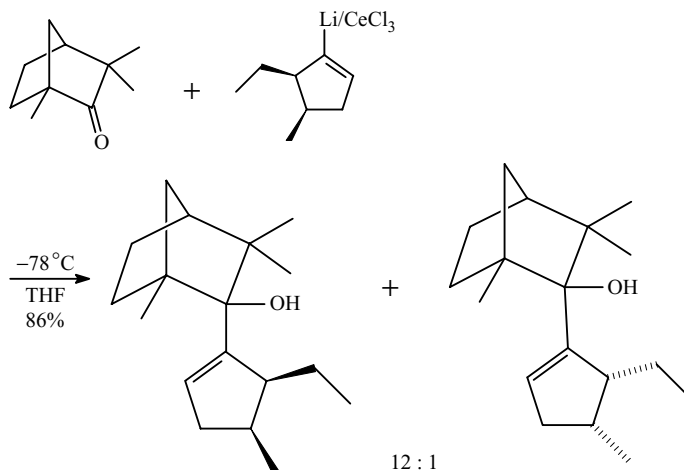
Reaction of ‘anhydrous’ cerium(III) chloride with RLi reagents affords organocerium compounds {The cerium chloride is prepared by heating CeCl<sub>3</sub>(H<sub>2</sub>O)<sub>7</sub> *in vacuo* up to 140 °C and is in fact a monohydrate [CeCl<sub>3</sub>(H<sub>2</sub>O)], see W.J. Evans, J.D. Feldman, and J.W. Ziller, *J. Am. Chem. Soc.*, 1996, **118**, 4581.} Reaction is carried out at –78 °C, as decomposition is rapid at 0 °C, especially if a  $\beta$ -hydrogen is present in the R group. The exact nature of the cerium species is uncertain.

Some characteristics and advantages of these species are:

- They readily react with carbonyl groups by nucleophilic attack, in the same way as RLi or Grignard species, but generally react more smoothly (as they are less basic reagents than the alternatives, so reactions are not complicated by deprotonation side-reactions). These reactions afford high-yield syntheses of alcohols, especially those that can be difficult to make by other routes.
- They do not react with other functional groups, such as halides, esters, epoxides, or amines.
- They are much less basic than RLi or Grignard reagents, and the reactions can be carried out on molecules that tend to undergo enolization, metal-halogen exchange, reduction, or pinacol coupling when RLi is used.
- They often work in highly hindered situations, where other reagents do not avail.
- Reaction with  $\alpha,\beta$ -unsaturated carbonyl compounds gives 1,2-addition compounds selectively.
- They afford high diastereoselectivity, often opposite to that obtained by use of RLi. Allyl-cerium reactants tend to react at the less substituted terminus of the allyl unit, in contrast to other allylmetallic nucleophiles, which tend to attack at the most substituted terminus of the allyl unit.
- They are cheap reactants (owing to the low cost of cerium compounds).

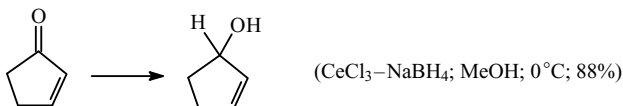


Reactions of chiral cycloalkenyl reagents with rigid ketones affords products with a high degree of stereodifferentiation:

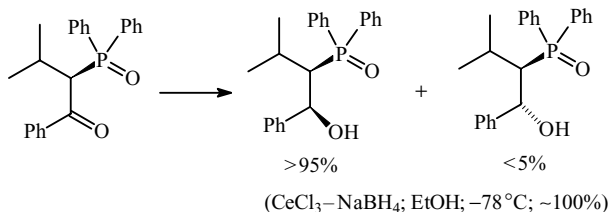


## 8.6 Cerium(III) Chloride and Metal Hydrides

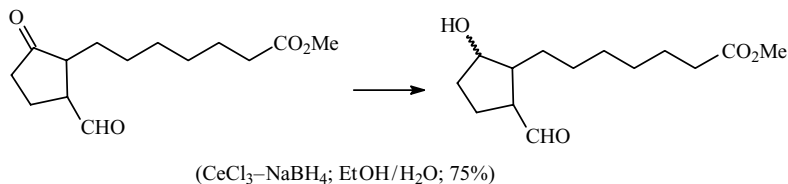
In combination with reducing agents ( $\text{NaBH}_4$ ,  $\text{LiAlH}_4$ ), cerium chloride modifies the reducing ability of the hydride. In combination with  $\text{NaBH}_4$ ,  $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$  selectively reduces the  $\text{C}=\text{O}$  group in enones, when use of  $\text{NaBH}_4$  by itself would give a mixture of allylic alcohols and saturated alcohols (the Luche reaction).



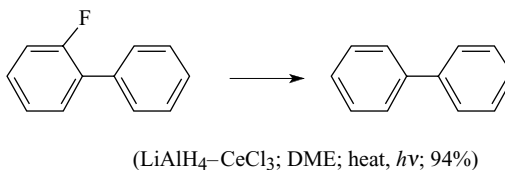
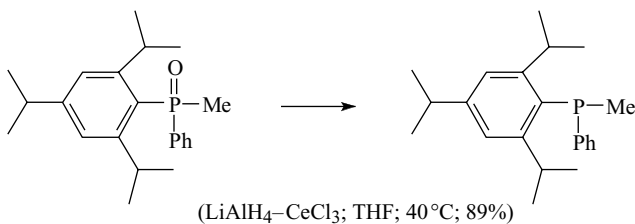
This mixture can be used for the stereoselective reduction of saturated ketones



and for the selective reduction of ketones in the presence of aldehydes, since, in alcoholic solution, the  $\text{Ce}^{3+}$  ion catalyses acetalization of aldehydes, protecting them from reduction.



A mixture of  $\text{LiAlH}_4$  and  $\text{CeCl}_3$  is a powerful reducing agent, reducing unsaturated carbonyl compounds to allylic alcohols (in this case, anhydrous cerium chloride is a necessity). It will reduce phosphine oxides to phosphines, oximes to primary amines, and  $\alpha,\beta$ -unsaturated carbonyl compounds to allylic alcohols. In particular, it reduces both aryl and alkyl halides to hydrocarbons.

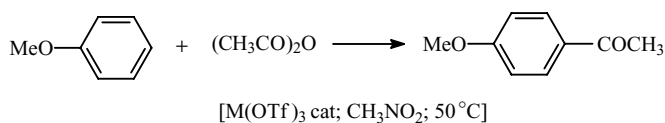


## 8.7 Scandium Triflate and Lanthanide Triflates

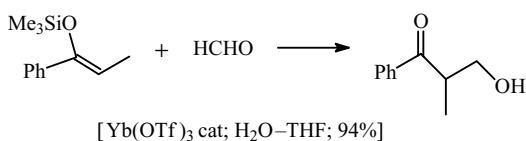
These reagents are associated especially with S. Kobayashi.  $\text{Ln}(\text{O}_3\text{SCF}_3)_3$  [ $\text{Ln}(\text{OTf})_3$ ] are synthesized in aqueous solution, crystallized as nonhydrates (Section 4.3.2) and the anhydrous triflates can be prepared by heating the hydrates. They are very effective Lewis acid catalysts, which perform well under mild conditions and can be used in both aqueous and organic solutions. Whilst most Lewis acids are decomposed in water (strictly dry organic solvents are employed in these reactions, cf.  $\text{AlCl}_3$  in Friedel–Crafts reactions), triflates are not affected. The ability to avoid the use of organic solvents gives triflates powerful ‘green’ credentials. They are catalysts for many reactions (Michael, Diels–Alder, allylation, Friedel–Crafts, imino–Diels–Alder, etc.). Scandium triflate has attracted especial attention, though the use of the cheaper ytterbium compound has also been well investigated.

### 8.7.1 Friedel–Crafts Reactions

Small amounts of  $\text{Sc}(\text{OTf})_3$  [as well as many  $\text{Ln}(\text{OTf})_3$ ] catalyse some Friedel–Crafts reactions. Unlike conventional Friedel–Crafts catalysts, there is no need to use stoichiometric amounts. The yield does depend upon the lanthanide; for example, in the following reaction, 89% (Sc), 55% (Yb), 28% (Y).

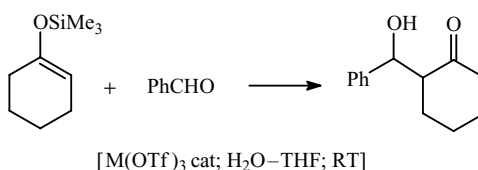


$\text{Yb}(\text{OTf})_3$  is an excellent catalyst for the aldol reactions of silylenol ethers with aldehydes in aqueous solution, working better than in organic solvents like THF and MeCN, though the reactions can also be performed in organic solvents, and, after the reaction has been quenched by the addition of water, the triflate catalyst may be recovered from the aqueous layer.



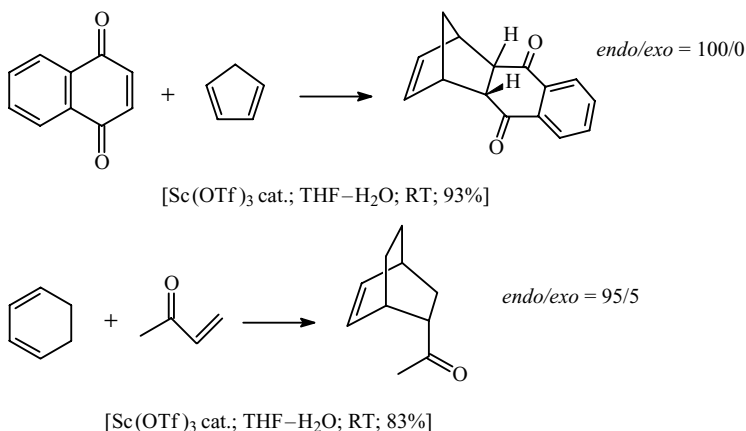
Even greater rates have been achieved in the  $\text{Yb}(\text{OTf})_3$ -catalysed aldol reactions of silylenol ethers with aldehydes in micelles, by adding a small quantity of surfactant, such as sodium dodecyl sulfate.

A study of the reaction of benzaldehyde with 1-(trimethylsilyloxy)cyclohexane shows a remarkable dependence of the yield upon the lanthanide used, being as high as 91% for  $\text{Yb}(\text{OTf})_3$  and as low as 8% with  $\text{La}(\text{OTf})_3$ .

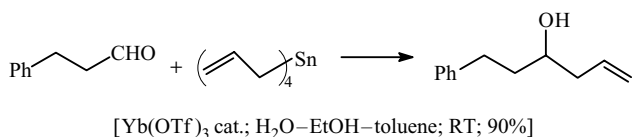


### 8.7.2 Diels–Alder Reactions

Lanthanide triflates catalyse Diels–Alder reactions, with the scandium complex as the most effective catalyst, and, again, the catalyst can be recovered and reused, being just as effective in subsequent runs.

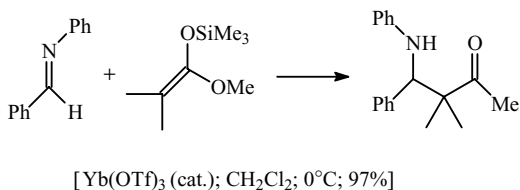


The triflates catalyse the allylation of carbonyl compounds with tetraallyltin, producing intermediates in the synthesis of higher sugars.



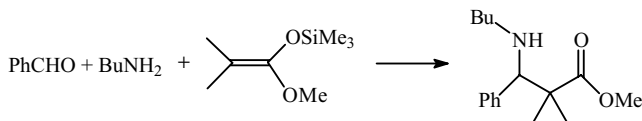
### 8.7.3 Mannich Reactions

Another synthesis to which they have been applied is Mannich-type reactions between imines and enolates (especially silyl enolates) to afford  $\beta$ -amino ketones or esters.



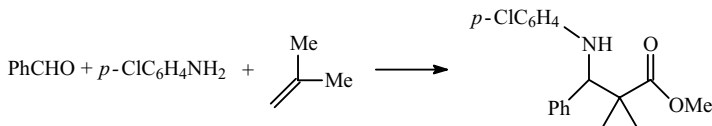
Since many imines are not stable enough for their isolation and purification, an extension of the previous synthesis lies in a one-pot reaction that reacts with *in situ* prepared imines

with silyl enolates to produce  $\beta$ -amino esters.



[Yb(OTf)<sub>3</sub> (cat.) + dehydrating agent; CH<sub>2</sub>Cl<sub>2</sub>; RT; 85%]

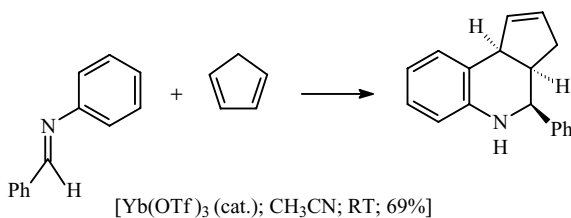
$\beta$ -Amino ketones can be made from an aldehyde, an amine, and a vinyl ether in a one-pot synthesis, an aqueous Mannich-type reaction.



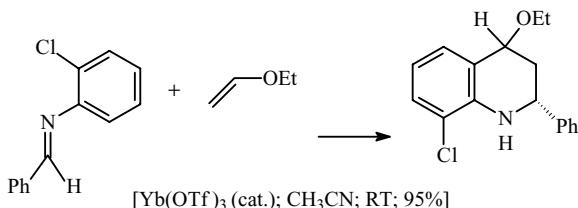
[Yb(OTf)<sub>3</sub> (cat.); THF-H<sub>2</sub>O; RT; 90%]

#### 8.7.4 Imino-Diels–Alder Reactions

Lanthanide triflates are catalysts for a powerful imino-Diels–Alder reaction for building N-containing six-membered heterocycles.

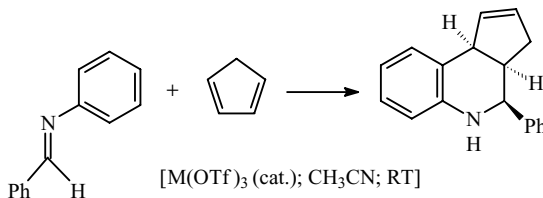


[Yb(OTf)<sub>3</sub> (cat.); CH<sub>3</sub>CN; RT; 69%]



[Yb(OTf)<sub>3</sub> (cat.); CH<sub>3</sub>CN; RT; 95%]

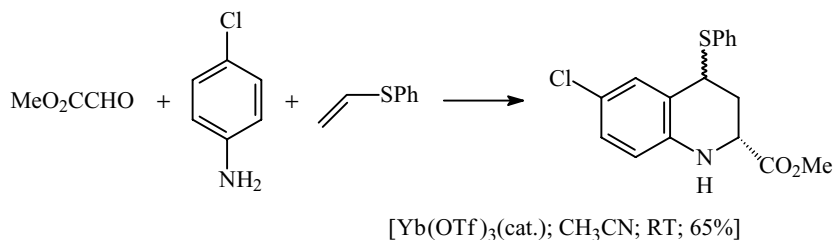
The yields again depend upon the choice of the lanthanide triflate. In a study of the reaction:



[M(OTf)<sub>3</sub> (cat.); CH<sub>3</sub>CN; RT]

best yields were obtained with heavy lanthanides such as Er (97%) and Yb (85%), in contrast to La (45%) and Pr (60%).

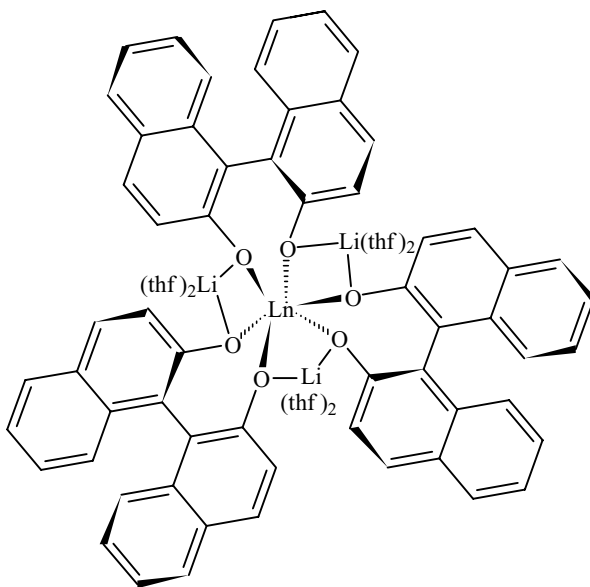
Another one-pot synthesis uses reaction of an aldehyde, an amine, and an alkene to give pyridine and quinoline derivatives via the imino-Diels–Alder route.



Extensions of the triflate catalyst include the use of versions with fluorinated ‘ponytails’ such as [Sc{C(SO<sub>2</sub>C<sub>8</sub>F<sub>17</sub>)<sub>3</sub>}<sub>3</sub>] for use in fluorous phase Diels–Alder reactions (fluorinated solvent.)

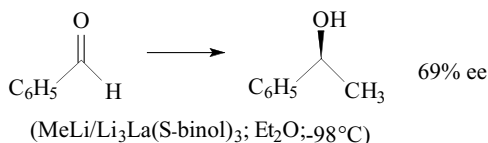
## 8.8 Alkoxides and Aryloxides

Complexes LnM<sub>3</sub>tris(binaphthoxide) (M = alkali metal) have a good deal of utility as catalysts.

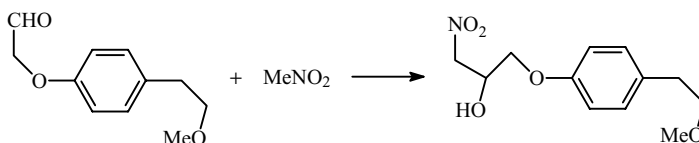


The lanthanide complexes are soluble in ethers like Et<sub>2</sub>O or THF. They are catalysts for the enantioselective reduction of aldehydes, with best results for the lanthanum complex. Thus the yield is 72% when M = La, but 50% when M = Yb; more strikingly, the enantiomeric excess is 69% for the La complex but only 3% when the Yb complex was

used.



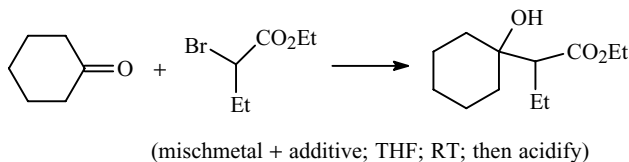
The research group of Shibasaki has studied similar compounds,  $\text{LnM}_3(\text{binaphthoxide})_3 \cdot x \text{ THF} \cdot y \text{ H}_2\text{O}$  ( $\text{M} = \text{Li}, \text{Na}, \text{K}$ ) as catalysts for a wide range of reactions, including epoxidation of enones, hydrophosphonylation of imines and aldehydes, and a range of asymmetric C–C bond-forming reactions (Diels–Alder, Michael addition, aldol and nitroaldol formation). Yields and enantioselectivity can depend markedly upon the alkali metal. Thus, in the nitroaldol reaction shown below, the yields are very similar (90, 92%) when  $\text{LnM}_3(\text{binaphthoxide})_3$  are used ( $\text{M} = \text{Li}, \text{Na}$ ), however the ee is 94% when using the Li compound but only 2% if the sodium compound is employed.



Lanthanide isopropoxides, usually written  $\text{Ln}(\text{OPr}^i)_3$ , but more likely to be oxo-centred clusters  $\text{Ln}_5\text{O}(\text{OPr}^i)_{13}$ , are used, not just as starting materials for the synthesis of catalysts such as the naphthoxides but also as catalysts in their own right. They have been used in the Meerwein–Ponndorf–Verley reaction, where carbonyl compounds are reduced to alcohols, recent studies having shown that the reaction takes place exclusively by a carbon-to-carbon hydrogen transfer.

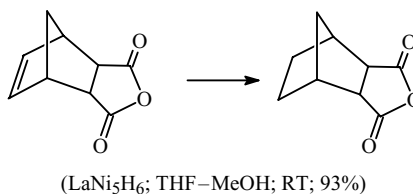
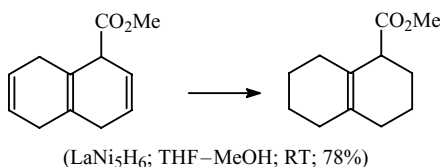
## 8.9 Lanthanide Metals

Apart from the role of mischmetal as a co-reductant in  $\text{SmI}_2$ -catalysed reactions such as pinacolization (Section 8.3.3) mischmetal has been found to be a useful reactant in its own right. Thus a combination of mischmetal and additives (1,2-diiodoethane or iodine) has been active in Reformatsky-type reactions. Though giving slightly lower yields than  $\text{SmI}_2$ , they are less air-sensitive; there is the further handicap of requiring slow (dropwise) addition of reactants.

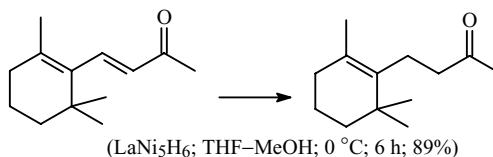


Lanthanum–nickel alloys are useful hydrogenation catalysts. The alloy  $\text{LaNi}_5$  readily absorbs large amounts of hydrogen. The catalysts are robust, hard to poison, are capable of repeated reuse, and operate under mild conditions.

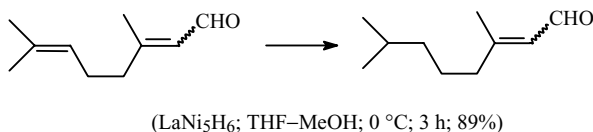




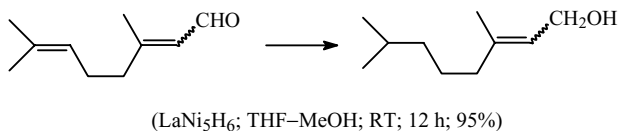
It selectively catalyses hydrogenation of C=C units (especially conjugated double bonds) but under more forcing conditions it also reduces other functional groups such as carbonyl, nitro, and nitrile.



Compare



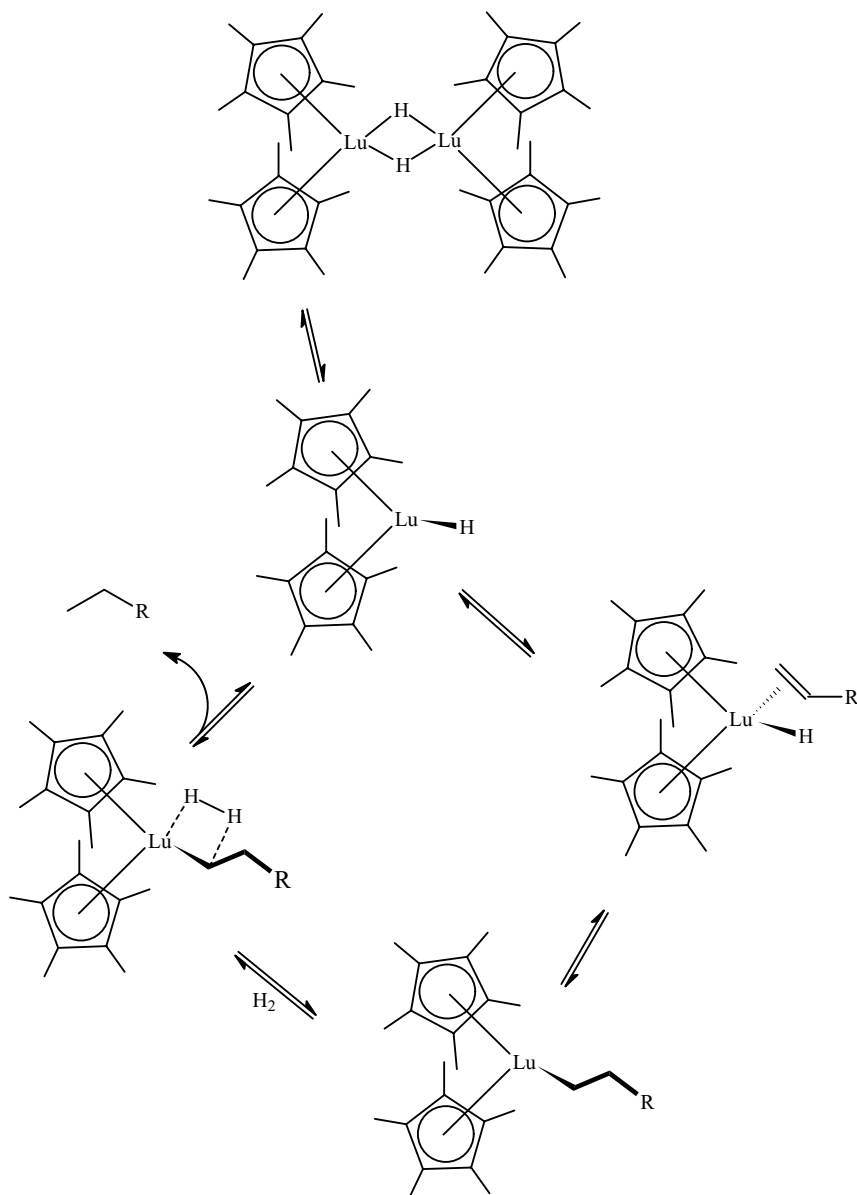
and



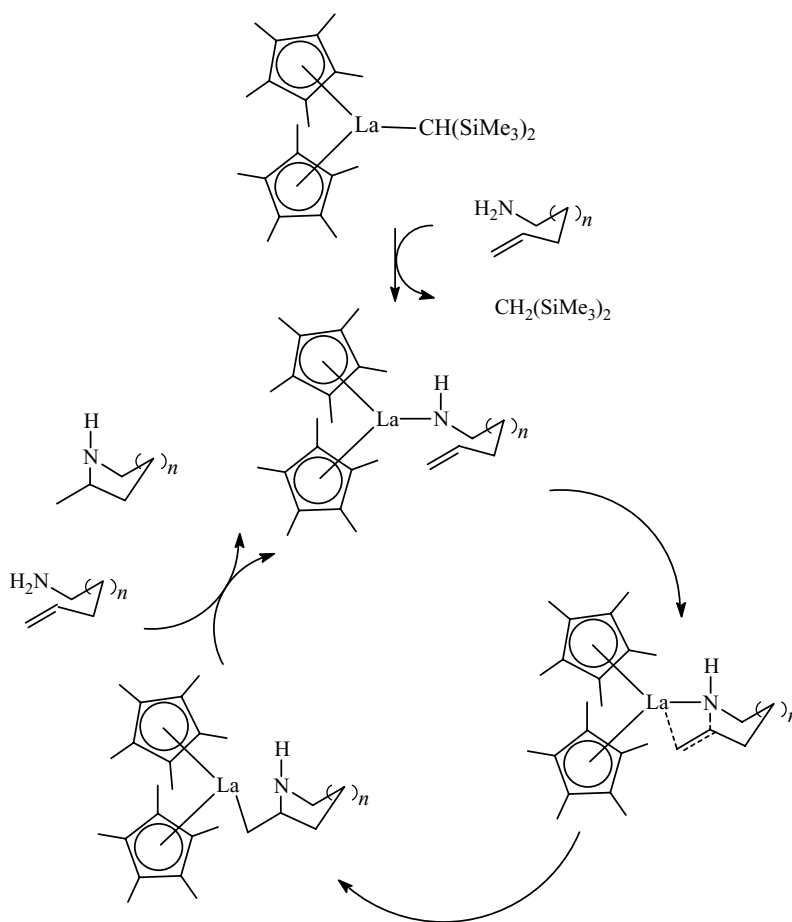
## 8.10 Organometallics and Catalysis

Considerable study is being made of the ability of organometallic compounds of the lanthanides (and actinides) to catalyse reactions of organic substrates, much of this work associated with the name of Tobin J. Marks. The hydride [Cp\*<sub>2</sub>Lu(μ-H)<sub>2</sub>LuCp\*<sub>2</sub>] (Cp\* = C<sub>5</sub>Me<sub>5</sub>) is an exceptionally active catalyst for the homogeneous hydrogenation of alkenes and alkynes. A suggested mechanism, involving dissociation to the coordinatively unsaturated monomer [Cp\*<sub>2</sub>LuH], is shown below (Figure 8.1) – readers will note a resemblance to the mechanism of hydrogenation using [RhCl(PPh<sub>3</sub>)<sub>3</sub>].

A whole range of reactions are catalysed by such complexes. Figure 8.2 shows the mechanism proposed in a recent study of hydroamination, catalysed by  $[\text{Cp}^*_2\text{La}\{\text{CH}(\text{SiMe}_3)_2\}_2]$ . It indicates a two-stage mechanism, cyclization to form La–C and C–N bonds, followed by La–C protonolysis. The alkene inserts into the La–C bond via a four-centre transition state, followed by protonolysis by a second substrate molecule and dissociation of the cyclized amine, which regenerates the catalyst. The rate-determining step involves a highly organised seven-membered chair-like cyclic transition state.



**Figure 8.1**  
Catalytic hydrogenation using  $[\text{Cp}^*_2\text{LuH}]$  catalyst.



**Figure 8.2**  
Hydroamination catalysed by  $[\text{Cp}^*_2\text{La}(\text{CH}(\text{SiMe}_3)_2)]$ .

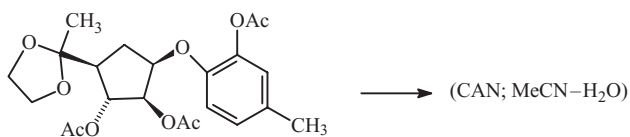
### Questions

- 8.1** How is  $\text{SmI}_2$  prepared? How may its activity be enhanced? What are the advantages to using it? What are the drawbacks to using it, and how can these be circumvented?
- 8.2** What are the main uses of lanthanide triflates? What are the advantages to using them?
- 8.3A** How are organocerium compounds prepared? Why are they useful? Why can  $\text{CeCl}_3/\text{NaBH}_4$  be used in the presence of water, whilst  $\text{CeCl}_3/\text{LiAlH}_4$  requires strictly anhydrous conditions?
- 8.3B** The complexes  $\text{LnM}_3\text{tris}(\text{binaphthoxide})$  ( $\text{M}$  = alkali metal) have a good deal of utility as catalysts (Section 8.3). They are readily prepared from either the appropriate lanthanide silylamide,  $\text{Ln}[\text{N}(\text{SiMe}_3)_2]_3$ , or chloride. Why choose the former, when the chloride can be bought ‘off the shelf’.

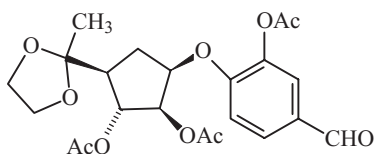
**Answer :** The former method has the advantage of a cleaner reaction, a lanthanide starting material soluble in common organic solvents, and chloride-free products.

## Problems

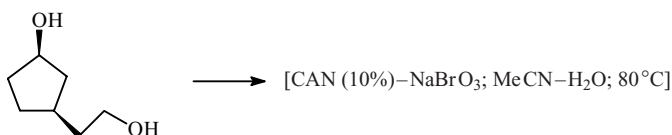
8.4 Suggest a product for:



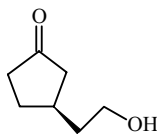
Answer:



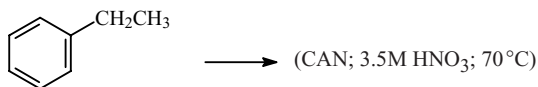
8.5 Suggest a product for:



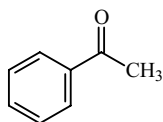
Answer:



8.6 Suggest a product for this reaction:

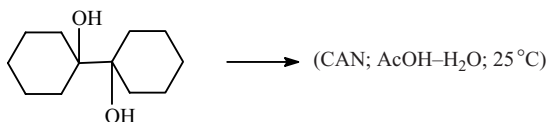


Answer:

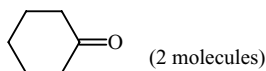


[G.A. Molander, *Chem. Rev.*, 1992, **92**, 29 (in particular, p. 31)].

8.7 Suggest a product of this reaction:

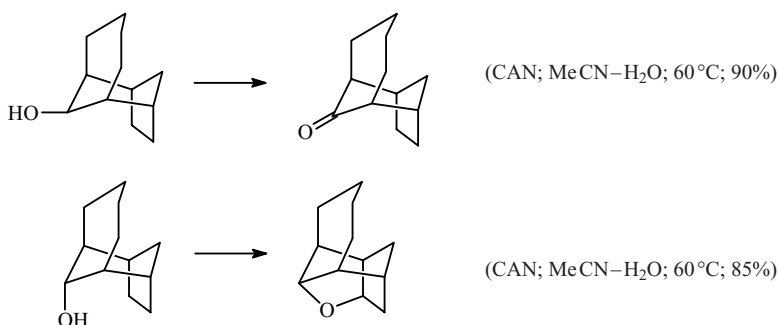


**Answer:**



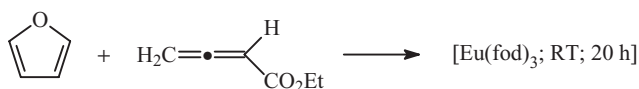
(T. Imamoto, *Lanthanides in Organic Synthesis*, Academic Press, 1994, p. 130; G.A. Molander, *Chem. Rev.* 1992, **92**, 29).

8.8 Explain the difference between these reactions:

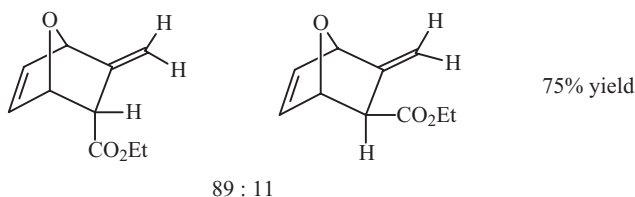


**Answer:** In one isomer, there is the possibility of delta-hydrogen abstraction by an alkoxyl radical, forming a furan ring; in the other, the alcohol group is too far away from the delta hydrogen for this to happen.

8.9 Predict the two products of:

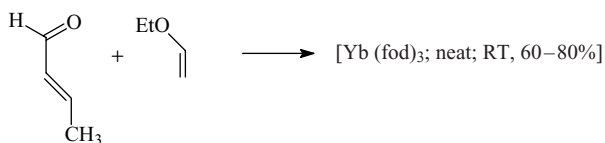


**Answer:**

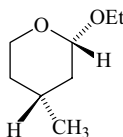


[G.A. Molander, *Chem. Rev.*, 1992, **92**, 29 (in particular, p. 60)].

**8.10** Predict the product of this reaction:

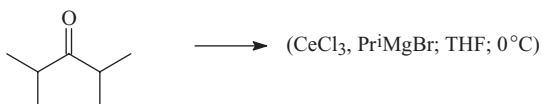


**Answer:**



(T. Imamoto 107, *Lanthanides in Organic Synthesis*, Academic Press, 1994, 107).

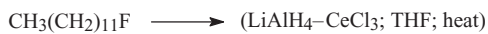
**8.11** Predict the product of this reaction:



**Answer:** (Pr<sup>i</sup>)<sub>3</sub>COH

G.A. Molander, *Chem. Rev.*, 1992, **92**, 29 [(in particular, p. 44)].

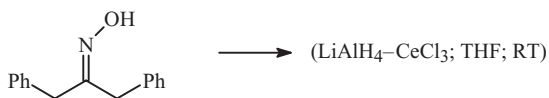
**8.12** Predict the product of this reaction:



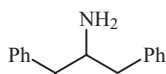
**Answer:** C<sub>12</sub>H<sub>26</sub>

[G.A. Molander, *Chem. Rev.*, 1992, **92**, 29 (in particular, p. 37)].

**8.13** Predict the product of this reaction:

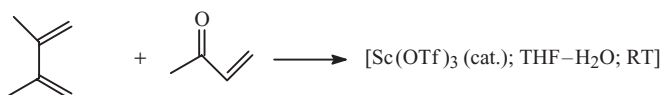


**Answer:**

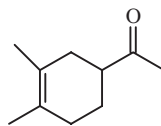


[G.A Molander, *Chem. Rev.*, 1992, **92**, 29 (in particular, p. 39)].

**8.14** Predict the product of this reaction:

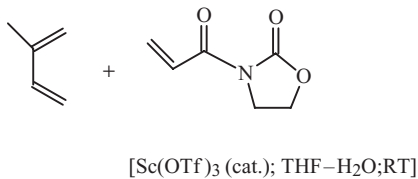


**Answer:**

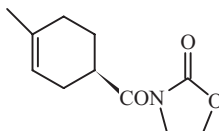


[S. Kobayashi (ed.) *Lanthanides: Chemistry and use in Organic Synthesis*, Springer-Verlag, Heidelberg, 1999, p. 78].

**8.15** Predict the product of this reaction:

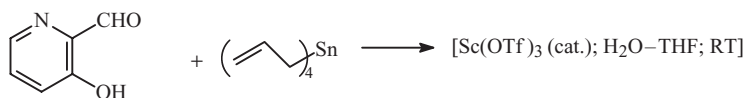


**Answer:**

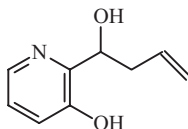


[S. Kobayashi (ed.) *Lanthanides: Chemistry and Use in Organic Synthesis*, Springer-Verlag, Heidelberg, 1999, p. 81].

**8.16** Predict the product of this reaction:

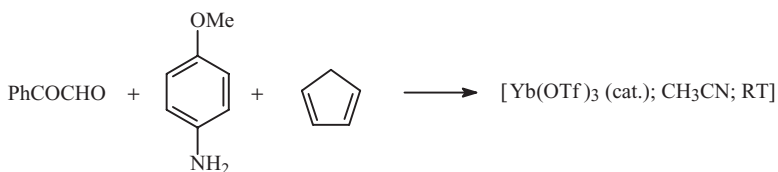


**Answer:**

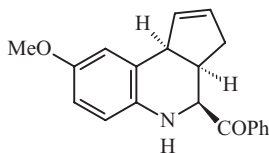


[S. Kobayashi (ed.) *Lanthanides: Chemistry and Use in Organic Synthesis*, Springer-Verlag, Heidelberg, 1999, p. 81].

**8.17** Predict the product of this reaction:



**Answer:**



[S. Kobayashi (ed.) *Lanthanides: Chemistry and Use in Organic Synthesis*, Springer-Verlag, Heidelberg, 1999, p. 95].





# 9 Introduction to the Actinides

By the end of this chapter you should be able to:

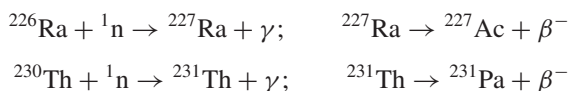
- recall that most of the actinides do not occur in nature, that all are radioactive, and that they have increasingly short half-lives as the series is traversed;
- understand the methods used to extract and synthesize them;
- understand isotopic separation processes and the need for them;
- recall that the early actinides exhibit transition-metal-like behaviour and that the later actinides resemble the lanthanides in their chemistry;
- explain the stability of the different oxidation states for the actinides;
- recognize +4 and +6 as the main oxidation states for uranium, and +4 as the only important state for thorium;
- recall that relativistic effects are significant in the chemistry of these elements.

## 9.1 Introduction and Occurrence of the Actinides

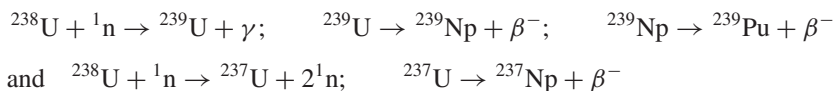
Although the first compounds of uranium and thorium were discovered in 1789 (Klaproth) /1828 (Berzelius), most of these elements are man-made products of the 20th century. Thorium and uranium are both long-lived and present in the earth in significant amounts, but for practical purposes the others should be regarded as man-made, though actinium and protactinium occur in nature in extremely small amounts, as decay products of  $^{235}\text{U}$  and  $^{238}\text{U}$ , whilst microscopic amounts of plutonium, generated through neutron capture by uranium, have been reported to occur naturally. The principal thorium ore is monazite, a phosphate ore also containing large amounts of the lanthanides, whilst the main uranium ore is  $\text{U}_3\text{O}_8$ , usually known as pitchblende. Elements beyond uranium are man-made and their synthesis is described in section 9.2. All the actinides are radioactive, sometimes intensely; this requires special care in their handling, and the radioactivity often plays a part in their chemistry, as in causing radiation damage in solutions and in dislocating the regular arrangements of particles in crystals.

## 9.2 Synthesis

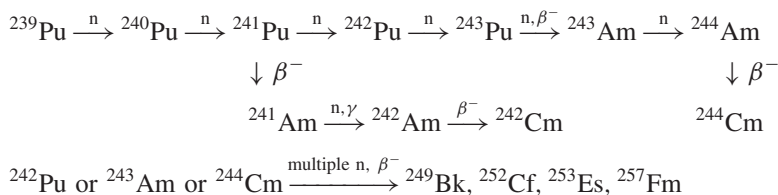
Apart from thorium, protactinium, and uranium, the actinides are obtained by a bombardment process of some kind. Thus for actinium (and also protactinium):



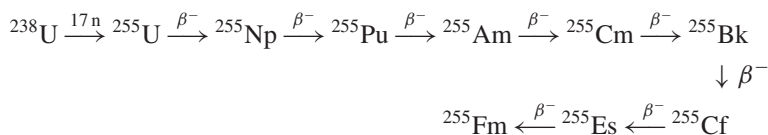
Similarly, for the elements directly beyond uranium:



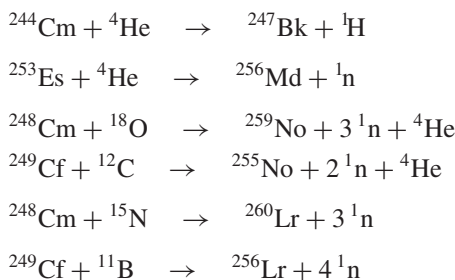
For elements beyond plutonium, successive neutron capture is required. This is, obviously, a slower process; thus starting with 1 kg of  $^{239}\text{Pu}$ , using a neutron flux of  $3 \times 10^{14}$  neutrons  $\text{cm}^{-2}\text{s}^{-1}$  (a high but experimentally feasible value), around 1 mg of  $^{252}\text{Cf}$  is obtained after 5–10 y.



The limit of this process in a reactor is  $^{257}\text{Fm}$ ; the product of the next neutron absorption is  $^{258}\text{Fm}$ , which undergoes spontaneous fission ( $t_{1/2} = 0.38$  ms). This point can be passed in two ways. One is to utilize a more intense neutron flux than can be obtained in a reactor, in the form of a thermonuclear explosion, so that a product such as  $^{258}\text{Fm}$  undergoes further neutron absorption before fission can occur. Here, in the synthesis of  $^{255}\text{Fm}$  in 'Ivy Mike', the world's first thermonuclear test, at Eniwetok atoll on 1st November 1952, the initial product of multiple neutron capture,  $^{255}\text{U}$ , underwent a whole series of rapid decays, yielding  $^{255}\text{Fm}$ .



For obvious reasons, this route is not likely to be followed in the future; instead, heavy-ion-bombardment, using particles such as  $^{11}\text{B}$ ,  $^{12}\text{C}$ , and  $^{16}\text{O}$ , will be used, though more recently heavier ones like  $^{48}\text{Ca}$  and  $^{56}\text{Fe}$  have been utilized. This route is reliable but has the twin drawbacks (from the point of view of yield) of requiring a suitable actinide target and also being an atom-at-a-time route. Examples include:



The most important and longest-lived isotopes are listed in Table 9.1.

**Table 9.1** Longest-lived isotopes of the actinide elements

	Mass	Half-life	Means of decay
Ac	227	21.77 y	$\beta^-$
Th	232	$1.41 \times 10^{10}$ y	$\alpha$
Pa	231	$3.28 \times 10^4$ y	$\alpha$
U	234	$2.45 \times 10^5$ y	$\alpha$
	235	$7.04 \times 10^8$ y	$\alpha$
	238	$4.47 \times 10^9$ y	$\alpha$
Np	236	$1.55 \times 10^5$ y	$\beta^-$ , EC
	237	$2.14 \times 10^6$ y	$\alpha$
Pu	239	$2.14 \times 10^4$ y	$\alpha$
	240	$6.57 \times 10^3$ y	$\alpha$
	242	$3.76 \times 10^5$ y	$\alpha$
	244	$8.26 \times 10^7$ y	$\alpha$
Am	241	432.7 y	$\alpha$
	243	$7.38 \times 10^3$ y	$\alpha$
Cm	244	18.11 y	$\alpha$
	245	$8.5 \times 10^3$ y	$\alpha$
	246	$4.73 \times 10^3$ y	$\alpha$
	247	$1.56 \times 10^7$ y	$\alpha$
	248	$3.4 \times 10^5$ y	$\alpha$
	250	$1.13 \times 10^4$ y	$\alpha$ , SF
Bk	247	$1.38 \times 10^3$ y	$\alpha$
	249	320 d	$\beta^-$
Cf	249	351 y	$\alpha$
	250	13.1 y	$\alpha$
	251	898 y	$\alpha$
	252	2.64 y	$\alpha$
Es	252	472 d	$\alpha$
	253	20.47 d	$\alpha$
	254	276 d	$\alpha$
	255	39.8 d	$\beta^-$
Fm	257	100.4 d	$\alpha$
Md	258	55 d	$\alpha$
No	259	1 h	$\alpha$ , EC
Lr	260	3.0 min	$\alpha$

## 9.3 Extraction of Th, Pa, and U

### 9.3.1 Extraction of Thorium

Thorium makes up around 10% of monazite; one process for its extraction relies on treating the ground ore with concentrated aq. NaOH at 240 °C for some hours, then adding hot water. This dissolves out  $\text{Na}_3\text{PO}_4$ , leaving a mixture of the hydrated oxides and hydroxides of the lanthanide and Th. On adjusting the pH to 3.5 with boiling HCl, the lanthanide oxides dissolve, leaving behind only hydrated  $\text{ThO}_2$ . This can be converted into  $\text{Th}(\text{NO}_3)_4$ , and purified by solvent extraction into kerosene with tributyl phosphate.

In the acid route, the phosphate ore is digested with sulfuric acid at 230 °C for some hours and thorium phosphate is precipitated on adjusting the pH to 1. This is purified by first converting it into  $\text{Th}(\text{OH})_4$ , thence into thorium nitrate, purified as above.

### 9.3.2 Extraction of Protactinium

First identified in 1913 (the first compound,  $\text{Pa}_2\text{O}_5$ , was isolated in 1927 by von Grosse, who isolated the element in 1931), protactinium is not generally extracted. Most of what is known about the chemistry of protactinium ultimately results from the extraction in 1960 by the UK Atomic Energy Authority of some 125 grams of Pa, from 60 tons of waste material left over from the extraction of uranium, at a cost of about \$500,000 (very roughly, £1,250,000 at today's exchange rate).

### 9.3.3 Extraction and Purification of Uranium

Uranium is deposited widely in the Earth's crust, hence it has few ores, notably the oxides uraninite and pitchblende. The ores are leached with  $\text{H}_2\text{SO}_4$  in the presence of an oxidizing agent such as  $\text{NaClO}_3$  or  $\text{MnO}_2$ , to oxidize all the uranium to the (+6) state as a sulfate or chloride complex. On neutralization with ammonia a precipitate of 'yellow cake', a yellow solid with the approximate composition  $(\text{NH}_4)_2\text{U}_2\text{O}_7$  is formed. This is converted into  $\text{UO}_3$  on ignition at 300 °C. This can be purified further by conversion into uranyl nitrate, followed by solvent extraction using tributyl phosphate in kerosene as the extractant.

## 9.4 Uranium Isotope Separation

Having purified the uranium, it is then treated to separate the  $^{235}\text{U}$  and  $^{238}\text{U}$  isotopes for nuclear fuel purposes (any uranium compounds purchased commercially are already depleted in  $^{235}\text{U}$ ). In practice, nuclear fuel requires enrichment from the natural abundance of 0.71 %  $^{235}\text{U}$  to around 5%, so what follows details a degree of enrichment not usually required.

The uranium compound usually used is  $\text{UF}_6$ . It is chosen on account of its volatility (sublimes at 56.5 °C) and low molecular mass ( $M_r$ ), despite its extreme sensitivity to moisture (and toxicity of the HF produced) requiring the use of scrupulously sealed and water-free conditions, as well as fluorine-resistant materials.

### 9.4.1 Gaseous Diffusion

$\text{UF}_6$  vapour diffuses through barriers ( $\text{F}_2$ -resistant Al or Ni) with pores of diameter *ca* 10–25 nm at 70–80 °C.

Applying Graham's Law dictates a separation factor,  $\alpha^*$ , where

$$\alpha^* = \sqrt{M_r(^{238}\text{UF}_6)/M_r(^{235}\text{UF}_6)} = \sqrt{352/349} = 1.00429$$

Consecutive stages are linked in a cascade to provide the desired degree of enrichment, with 3000 stages giving up to 90% enrichment in  $^{235}\text{U}$ . A great deal of energy is needed to pump the  $\text{UF}_6$  round the system.

### 9.4.2 Gas Centrifuge

On centrifuging  $\text{UF}_6$  vapour in a gas centrifuge,  $^{238}\text{UF}_6$  tends to concentrate towards the outside of the centrifuge whilst the lighter  $^{235}\text{UF}_6$  predominates near the axis of the centrifuge. Better separations are achieved at high speeds and temperatures, and an advantage of the process is that the separation is in direct proportion to  $M_r$ .

9.4.3 Electromagnetic Separation

Ionized  $\text{UCl}_4$  was separated using a cyclotron-like system to obtain the first enriched samples used in the Manhattan project. In practice, this was a difficult method to utilize and was rejected in favour of gaseous diffusion.

9.4.4 Laser Separation

One process has involved selectively ionizing  $^{235}\text{U}$  in uranium vapour using a tuneable laser. In another process (Figure 10.6),  $^{235}\text{UF}_6$  molecules in a gaseous mixture are selectively ionized using an IR laser (the isotope shift of  $\nu$  U-F is around  $0.5\text{ cm}^{-1}$ ); the excited  $^{235}\text{UF}_6$  molecules are decomposed by a UV laser to give solid  $\text{UF}_5$ ; the  $^{238}\text{UF}_6$  molecules are unaffected. Low temperatures are used to give sharp absorption bands so that the vibration of the  $^{235}\text{UF}_6$  molecules but not that of the  $^{238}\text{UF}_6$  molecules is activated. Decomposition of  $\text{U(OMe)}_6$  has also been studied.

9.5 Characteristics of the Actinides

Table 9.2 depicts the oxidation states of the actinides. For the early actinides, Ac–Np, the highest (though not necessarily the most stable) oxidation state reflects the total number of electrons (6d and 5f) that can be removed from the outer shell. This resemblance to the transition metals was noted for Ac–U nearly a century ago and initially made people think that the actinides were another block of transition metals. Later, starting round about Bk, most elements tend to exhibit one stable oxidation state, +3 in nearly all cases, thus resembling the lanthanides.

Table 9.2 Oxidation states of the actinides

	2+	3+	4+	5+	6+	7+
Ac						
Th	?					
Pa						
U						
Np						
Pu						
Am						?
Cm					?	
Bk						
Cf						
Es			?			
Fm						
Md						
No						
Lr						
Known						
Common						

**Table 9.3** Electron configurations of the actinides and their ions<sup>a</sup>

	M	M <sup>3+</sup>	M <sup>4+</sup>
Ac	6d <sup>1</sup> 7s <sup>2</sup>		
Th	6d <sup>2</sup> 7s <sup>2</sup>	5f <sup>1</sup>	
Pa	5f <sup>2</sup> 6d <sup>1</sup> 7s <sup>2</sup>	5f <sup>2</sup>	5f <sup>1</sup>
U	5f <sup>3</sup> 6d <sup>1</sup> 7s <sup>2</sup>	5f <sup>3</sup>	5f <sup>2</sup>
Np	5f <sup>4</sup> 6d <sup>1</sup> 7s <sup>2</sup>	5f <sup>4</sup>	5f <sup>3</sup>
Pu	5f <sup>6</sup> 7s <sup>2</sup>	5f <sup>5</sup>	5f <sup>4</sup>
Am	5f <sup>7</sup> 7s <sup>2</sup>	5f <sup>6</sup>	5f <sup>5</sup>
Cm	5f <sup>7</sup> 6d <sup>1</sup> 7s <sup>2</sup>	5f <sup>7</sup>	5f <sup>6</sup>
Bk	5f <sup>9</sup> 7s <sup>2</sup>	5f <sup>8</sup>	5f <sup>7</sup>
Cf	5f <sup>10</sup> 7s <sup>2</sup>	5f <sup>9</sup>	5f <sup>8</sup>
Es	5f <sup>11</sup> 7s <sup>2</sup>	5f <sup>10</sup>	5f <sup>9</sup>
Fm	5f <sup>12</sup> 7s <sup>2</sup>	5f <sup>11</sup>	5f <sup>10</sup>
Md <sup>b</sup>	5f <sup>13</sup> 7s <sup>2</sup>	5f <sup>12</sup>	5f <sup>11</sup>
No <sup>b</sup>	5f <sup>14</sup> 7s <sup>2</sup>	5f <sup>13</sup>	5f <sup>12</sup>
Lr <sup>b</sup>	5f <sup>14</sup> 6d <sup>1</sup> 7s <sup>2</sup>	5f <sup>14</sup>	5f <sup>13</sup>

<sup>a</sup>Configurations are in addition to a radon 'core' 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>2</sup> 3p<sup>6</sup> 3d<sup>10</sup> 4s<sup>2</sup> 4p<sup>6</sup> 4d<sup>10</sup> 4f<sup>14</sup> 5s<sup>2</sup> 5p<sup>6</sup> 5d<sup>10</sup> 6s<sup>2</sup> 6p<sup>6</sup>

<sup>b</sup>Predicted

Early in the actinide series, electrons in the 6d orbitals are lower in energy than there is 5f orbitals. This is clear from the ground-state electronic configurations (Table 9.3) of the atoms, which show that the 6d orbitals are filled before 5f. The 5f orbitals are starting to be filled at protoactinium, and with the exception of curium, the 6d orbitals are not occupied again.

The 5f orbitals are not shielded by the filled 6s and 6p subshells as the 4f orbitals of the lanthanides are (by the corresponding 5s and 5p subshells). Moreover, the energy gap between 5f<sup>n</sup> 7s<sup>2</sup> and 5f<sup>n-1</sup> 6d 7s<sup>2</sup> configurations is less than for the corresponding lanthanides. Not only are the 5f orbitals less 'inner orbitals' in the sense that the 4f orbitals are for the lanthanides, and thus more perturbed in bonding, but the near-degeneracy of the 5f, 6d, and 7s electrons means that more outer-shell electrons can be involved in compound formation (and a wider range of oxidation states observed). Thus, the first four ionization energies of Th are 587, 1110, 1978, and 2780 kJ mol<sup>-1</sup> (Table 9.4) compared with respective values for Zr of 660, 1267, 2218, and 3313 kJ mol<sup>-1</sup>. So, for the earlier actinides, higher oxidation states are available and, as for the d block, several are often available for each metal [relativistic effects may also be important (Section 9.7)]. However, as the 5f electrons do not shield each other from the nucleus effectively, the energies of the 5f orbitals drop rapidly with increasing atomic number, so that the electronic structures of the later actinides and their ions become more and more like those of the lanthanides, whose chemistry they thus resemble.

## 9.6 Reduction Potentials of the Actinides

Although a full range of ionization energies is not available throughout the actinide series and thus cannot be used predictively, as for the lanthanides (Table 2.2), electrode potentials are more generally available (Table 9.5) and thus can be so used, as follows:

**Table 9.4** Ionization energies of the actinides (kJ/mol)

	$I_1$	$I_2$	$I_3$	$I_4$
Ac	499	1170	1900	4700
Th	587	1110	1978	2780
Pa	568	1128		2991
U	584	1420	1900	3145
Np	597	1128	1997	3242
Pu	585	1128	2084	3338
Am	578	1158	2132	3493
Cm	581	1196	2026	3550
Bk	601	1186	2152	3434
Cf	608	1206	2267	3599
Es	630	1216	2334	3734
Fm	627	1225	2363	3792
Md	635	1235	2470	3840
No	642	1254	2643	3956
Lr	444	1428	2228	4910

**Table 9.5** Reduction potentials of the actinides (V)

	$M^{3+} + 3e \rightarrow M$	$M^{4+} + 4e \rightarrow M$	$M^{3+} + e \rightarrow M^{2+}$	$M^{4+} + e \rightarrow M^{3+}$
Ac	-2.13		-4.9	
Th		-1.83	-4.9	-3.7
Pa		-1.47	-4.7	-2
U	-1.8	-1.38	-4.7	-0.63
Np	-1.79	-1.30	-4.7	0.15
Pu	-2.03	-1.25	-3.5	0.98
Am	-2.07	-0.90	-2.3	2.3
Cm	-2.06		-3.7	3.1
Bk	-1.96		-2.8	1.64
Cf	-1.91		-1.6	3.2
Es	-1.98		-1.6	4.5
Fm	-2.07		-1.1	4.9
Md	-1.74		-0.15	5.4
No	-1.26		1.45	6.5
Lr	-2.1			7.9

1. The negative reduction potentials for the  $M^{3+}/M$  potentials indicate that the process



is energetically favourable, suggesting that the metals should react well with dilute acid (and possibly water too), as is in fact observed.

2. The large negative reduction potentials for the  $M^{3+}/M^{2+}$  process early in the series indicate that for these metals no aqueous chemistry of  $M^{2+}$  ions is to be expected. The potentials become less negative with increasing atomic number, indicating increasing stability of  $M^{2+}$ , and the positive value for No is in keeping with  $No^{2+}$  being the most stable ion for this metal in aqueous solution (Table 9.2). A number of compounds have been isolated in the solid state for  $Am^{2+}$  ( $5f^7$ ),  $Cf^{2+}$ , and  $Es^{2+}$  (as might be expected from the reduction potentials) and the (+2) ion is known in solution for Fm and Md too (Table 9.2).



3. The large negative values of  $E^\circ$  for  $M^{4+}/M^{3+}$  for Th and Pa indicate that reduction to form (+3) species for these metals will be difficult, whilst for U, Np, and Pu the smaller  $E^\circ$  values indicate that both the +3 and +4 states will have reasonable stability. However, from Am onwards,  $E^\circ > 2V$  for all these elements (except Bk), suggesting that for all these metals the (+3) state will be more favoured (as observed). The tendency for the  $E^\circ$  values for both  $M^{4+}/M^{3+}$  and  $M^{3+}/M^{2+}$  to become more positive, and for the reduction to be more favoured, on crossing the series from left to right, shows that overall the lower oxidation states become more stable the higher the atomic number.

## 9.7 Relativistic Effects

For the lighter chemical elements, the velocity of the electrons is negligible compared with the velocity of light. However, for the actinides and to a lesser extent the lanthanides this is not the case; as the velocity of the electrons increases towards  $c$ , then their mass increases too.

For a 1s electron in a uranium atom, the average radial velocity,  $V_{\text{rad}} = 92c/137$ ,  $\sim 0.67c$ . The mass increase is given by  $m = m_e/\sqrt{1 - 0.67^2} = 1.35 m_e$ . This produces a contraction of the 1s orbital and stabilization of 1s electrons. Electrons in other s shells also tend to be stabilized owing to their orthogonality with 1s. Similar but smaller effects occur for p electrons. In contrast, d and f electrons tend to be expanded and destabilized (compared with imaginary, ‘non-relativistic’ atoms), due to the increased shielding of the nucleus by the (increasingly stabilized) outer core s and p electrons. Since f electrons are poor at screening other electrons from the nuclear charge, then as the 4f shell is filled, there is a contraction of the 5p and 6s orbitals.

A important ‘relativistic effect’ is that 5f orbitals of actinides are larger and their electrons more weakly bound than predicted by non-relativistic calculations, hence the 5f electrons are more chemically ‘available’. This leads to:

- (a) a bigger range of oxidation states than with the lanthanides;
- (b) a greater tendency to covalent bond formation (but maybe involving 6d rather than 5f orbitals) in ions like  $MO_2^+$  and  $MO_2^{2+}$  (most notably the uranyl ion,  $UO_2^{2+}$ ).

**Question 9.1**  $4.5 \times 10^9$  tonnes of uranium is present in the Earth’s oceans, at a concentration of  $3.3 \text{ mg m}^{-3}$  (about 1/1000th that in the crust). How might it be extracted?

**Answer 9.1** Ion-exchange technology is a possibility. The main cost would be that of pumping all the water needed; wave energy technology (as part of a power station?) could be an answer. Recovering other valuable metals (e.g. gold) at the same time might also improve the economics.

**Question 9.2** What are the advantages of using  $UF_6$  for isotope separation?

**Answer 9.2** It vapourizes at low temperatures, so that little energy is used for that; it has a low molecular mass, so that, since separation factors are proportional to the difference in mass between the  $^{235}\text{U}$ - and  $^{238}\text{U}$ -containing molecules, easier separations are achieved; since fluorine is monoisotopic ( $^{19}\text{F}$ ), only molecules of two different masses are involved, minimizing overlap between  $^{235}\text{U}$ - and  $^{238}\text{U}$ -containing species (this would not be the case if, say, Cl or Br were involved).

**Question 9.3** What are the patterns in oxidation states seen in (a) the early actinides Ac–Pu and (b) the later ones, Am–Lr. With which parts of the Periodic Table are resemblances most pronounced? How does this relate to the electronic structure?

**Answer 9.3** (a) The maximum oxidation state observed for Ac–Np corresponds to the number of ‘outer-shell’ electrons. Similar behaviour is seen in transition-metal chemistry, for example for the metals Sc–Mn in the 3d series.

(b) Especially from Bk onwards, the elements exhibit one common oxidation state, +3 in almost all cases, resembling the lanthanides in that respect.



# 10 Binary Compounds of the Actinides

By the end of this chapter you should be able to:

- suggest syntheses for typical compounds;
- recognize patterns in formulae and explain them;
- recognize patterns in the stability of halides;
- recognize and explain trends in the volatility and coordination number in uranium halides;
- state why the properties of  $\text{UF}_6$  make it suitable for isotope separation;
- suggest properties for compounds;
- appreciate problems in the synthesis of halides of the heavier actinides;
- understand the structures of the actinide halides.

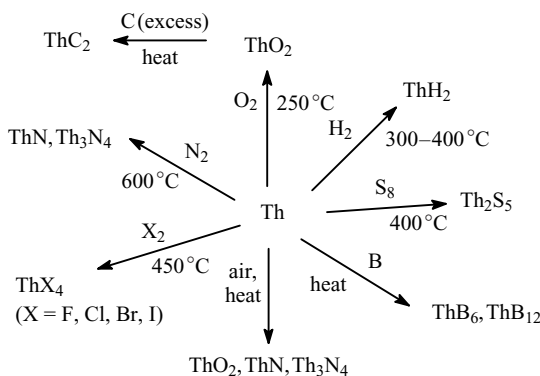
## 10.1 Introduction

This chapter examines some of the most important binary compounds of the actinides, especially the halides. Despite the problems caused by their radioactivity, some binary compounds of most of these elements have been studied in considerable detail, and form a good vehicle for understanding trends in the actinide series.

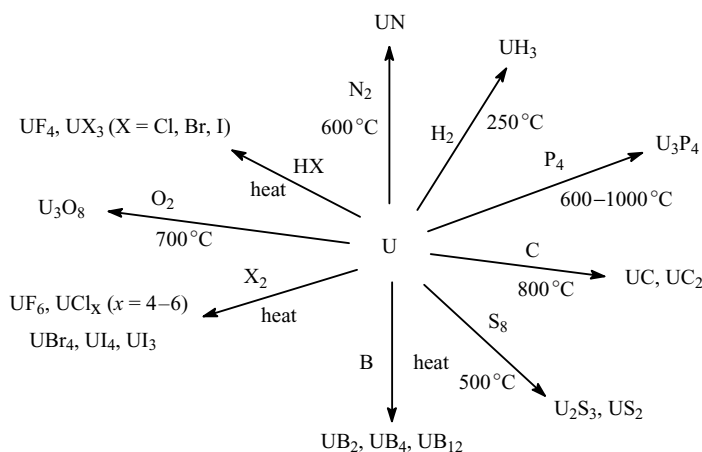
The actinides are reactive metals, typified by the reactions of thorium and uranium shown in Figures 10.1 and 10.2. These binary compounds frequently have useful properties. Thus, choosing examples from thorium chemistry,  $\text{Th}_2\text{S}_3$  is a high-temperature crucible material,  $\text{ThN}$  is a superconductor, and  $\text{Th}_3\text{P}_4$  and  $\text{Th}_3\text{As}_4$  are semiconductors.

## 10.2 Halides

The compounds known are summarized in Table 10.1. The only compound of an early actinide in the +2 state is  $\text{ThI}_2$ , a metallic conductor which is probably  $\text{Th}^{4+}(\text{e}^-)_2(\text{I}^-)_2$ . Certain heavier actinides form  $\text{MX}_2$  (Am, Cf, Es), which usually have the structure of the corresponding  $\text{EuX}_2$  and are thus genuine  $\text{M}^{2+}$  compounds. All four trihalides exist for all the actinides as far as Es, except for thorium and protactinium. Tetrafluorides exist for Th–Cm and the other tetrahalides as far as  $\text{NpX}_4$  (and in the gas phase in the case of  $\text{PuCl}_4$ ). Pentahalides are only known for Pa, U, and Np; whilst there are a few  $\text{MF}_6$  ( $\text{M} = \text{U}–\text{Pu}$ ), uranium is the only actinide to form a hexachloride. The known actinide halides are generally stable compounds; most are soluble in (and hydrolysed by) water.



**Figure 10.1**  
Reactions of thorium.



**Figure 10.2**  
Reactions of Uranium.

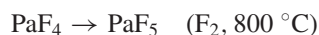
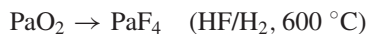
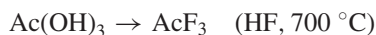
The maximum oxidation state found in compounds of the early actinides corresponds to the total number of electrons available in the 7s, 6d, and 5f orbitals. Beyond uranium this is no longer the case, and the stability of the high oxidation states decreases sharply; this probably reflects the decreasing availability of the 5f electrons for bonding. By the second half of the series, one oxidation state (+3) dominates, in the way observed for the lanthanides. Fluorine, the strongest oxidizing agent among the halogens, supports the highest oxidation states, as is generally observed elsewhere.

### 10.2.1 Syntheses of the halides

A considerable number of synthetic routes are available, many involving reaction of the oxides with HX or X<sub>2</sub> (according to the oxidation state desired) though sometimes more unusual halogenating agents like AlX<sub>3</sub> or hexachloropropene have been used. A selection of methods follow.

**Table 10.1** Oxidation states and halides of the actinides

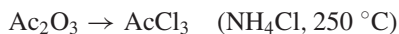
Oxidation state	2	3	4	5	6
Ac		F Cl Br I			
Th	I	I	F Cl Br I		
Pa		I	F Cl Br I	F Cl Br I	
U		F Cl Br I	F Cl Br I	F Cl Br	F Cl
Np		F Cl Br I	F Cl Br I	F	F
Pu		F Cl Br I	F		F
Am	Cl Br I	F Cl Br I	F		F?
Cm		F Cl Br I	F		F?
Bk		F Cl Br I	F		
Cf	Cl Br I	F Cl Br I	F		
Es	Cl Br I	F Cl Br I	F?		
Fm					
Md					
No					
Lr					

*Fluorides*

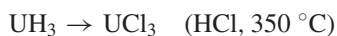
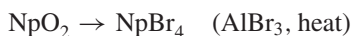
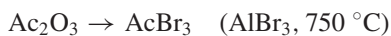
In some cases, where the +3 state is easily oxidized, a reductive route is used:

*Chlorides*

In the case of  $\text{AnCl}_3$ , the route used for lanthanide trihalides involving heating the oxide or hydrated chloride with ammonium chloride works well:



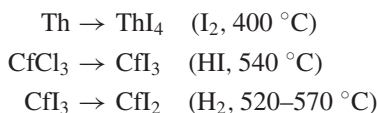
Again, reductive methods are sometimes necessary:

*Bromides*

**Table 10.2** Coordination number and structure types of the actinide trihalides

	C.N.	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
Fluorides	11	LaF <sub>3</sub>			LaF <sub>3</sub>	LaF <sub>3</sub>	LaF <sub>3</sub>	LaF <sub>3</sub>	LaF <sub>3</sub>	LaF <sub>3</sub>	LaF <sub>3</sub>					
	9									YF <sub>3</sub>	YF <sub>3</sub>					
Chlorides	9	UCl <sub>3</sub>			UCl <sub>3</sub>	UCl <sub>3</sub>	UCl <sub>3</sub>	UCl <sub>3</sub>	UCl <sub>3</sub>	UCl <sub>3</sub>	UCl <sub>3</sub>					
	8									PuBr <sub>3</sub>	PuBr <sub>3</sub>	PuBr <sub>3</sub>				
	6															
Bromides	9	UCl <sub>3</sub>			UCl <sub>3</sub>	UCl <sub>3</sub>										
	8					PuBr <sub>3</sub>	PuBr <sub>3</sub>	PuBr <sub>3</sub>	PuBr <sub>3</sub>	PuBr <sub>3</sub>						
	6									AlCl <sub>3</sub>	AlCl <sub>3</sub>	AlCl <sub>3</sub>				
	6									BiI <sub>3</sub>	BiI <sub>3</sub>					
Iodides	8			PuBr <sub>3</sub>	PuBr <sub>3</sub>	PuBr <sub>3</sub>	PuBr <sub>3</sub>									
	6							BiI <sub>3</sub>	BiI <sub>3</sub>	BiI <sub>3</sub>	BiI <sub>3</sub>	BiI <sub>3</sub>				

### Iodides



## 10.2.2 Structure Types

Trihalides are known for most of the actinides and form the basis for comparison with the lanthanides. Table 10.2 lists the known structures adopted by the trihalides.

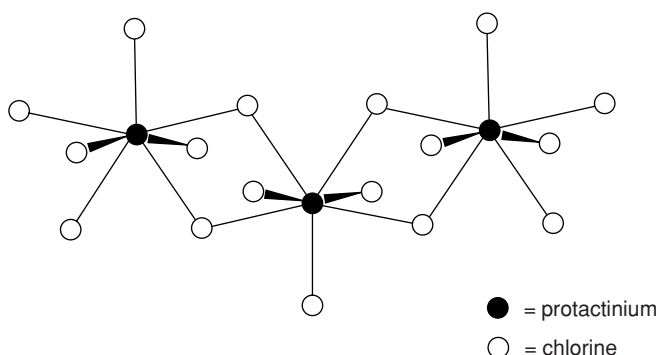
Of these structure types, the LaF<sub>3</sub> structure has a fully capped trigonal prismatic structure with 11 coordination (9 + 2); the YF<sub>3</sub> structure has rather distorted tricapped trigonal prismatic 9 coordination; the UCl<sub>3</sub> structure is a tricapped trigonal prism, from which the 8-coordinate PuBr<sub>3</sub> structure is derived by removing one of the face-capping halogens; the AlCl<sub>3</sub> and BiI<sub>3</sub> structures both have octahedral six-coordination.

The actinide trihalides display a similar pattern of structure to those of the lanthanide trihalides. However, comparing the coordination numbers for Ln<sup>3+</sup> and An<sup>3+</sup> ions with the same number of f electrons ('above one another in the Periodic Table'), it can be seen that the coordination number of the lanthanide halides decreases sooner than in the actinide series, a reflection of the fact that the larger actinide ions allow more halide ions to pack around them. Table 10.3 gives comparative coordination numbers for the trihalides of the lanthanides and actinides.

The tetrahalides have coordination numbers of 8 in the solid state whilst the pentahalides have 6 and 7 coordination. Thus PaF<sub>5</sub> and PaCl<sub>5</sub> are both seven coordinate (Figure 10.3),

**Table 10.3** Comparison of coordination for trihalide structures

	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
LnF <sub>3</sub>	11	11	11	11	11	11, 9	11, 9	9	9	9	9	9	9	9	9
LnCl <sub>3</sub>	9	9	9	9	9	9	9	9	8	6	6	6	6	6	6
LnBr <sub>3</sub>	9	9	9	8	8	8	8	6	6	6	6	6	6	6	6
LnI <sub>3</sub>	8	8	8	8	8	6		6	6	6	6	6	6	6	6
	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
AnF <sub>3</sub>	11			11	11	11	11	11	11, 9	11, 9					
AnCl <sub>3</sub>	9			9	9	9	9	9	9, 8	9, 8	8				
AnBr <sub>3</sub>	9			9	9, 8	8	8	8	8, 6	6	6				
AnI <sub>3</sub>			8	8	8	8	6	6	6	6	6				



**Figure 10.3**  
The chain structure adopted by  $\text{PaCl}_5$ .

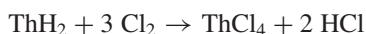
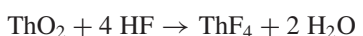
whilst  $\text{PaBr}_5$  is six coordinate; in contrast  $\text{UF}_5$  is seven coordinate (as is  $\text{NpF}_5$ ), whilst  $\text{UBr}_5$  and  $\text{UCl}_5$  are both six coordinate. Hexafluorides are formed by U–Pu (and just possibly Am),  $\text{UCl}_6$  is the only hexachloride; all  $\text{MX}_6$  are octahedral.

The properties and structures of the halides are mainly exemplified in this chapter by a consideration of the halides of thorium and uranium.

### 10.3 Thorium Halides

Apart from two rather ill-defined iodides in the +2 and +3 oxidation states, thorium forms exclusively halides in the +4 state. Heating thorium metal with  $\text{ThI}_4$  affords  $\text{ThI}_2$  and  $\text{ThI}_3$ , the latter not well characterized.  $\text{ThI}_2$  exists in black and gold forms; the high conductivity suggests that, like some of the apparent lanthanide(II) iodides (Section 3.3.3), it contains free electrons and is in fact  $\text{Th}^{4+} (\text{e}^-)_2 (\text{I}^-)_2$ .

The  $\text{Th}^{\text{IV}}$  halides can be made by various routes including:



All are white solids. Table 10.4 summarizes the structures of the thorium(IV) halides (the chloride and the bromide exist in two different forms in the solid state).

Thorium halides form many complexes with neutral donors, discussed in chapter 11. Here it may be noted that there are a number of anionic complexes, including  $\text{Cs}_2\text{ThCl}_6$ ,  $(\text{pyH})_2\text{ThBr}_6$ , and  $(\text{Bu}_4\text{N})_2\text{ThI}_6$ , which generally seem to contain isolated  $[\text{ThX}_6]^{2-}$

**Table 10.4** Thorium(IV) halides





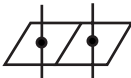
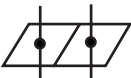








	Coord. No.	Solid state	Closest polyhedron	Gas phase	
		Bond length (Å)		Coord. No.	Bond length (Å)
$\text{ThF}_4$	8	2.30–2.37	Dodecahedron	4	2.14
$\text{ThCl}_4$	8	2.72–2.90 ( $\beta$ ); 2.85–2.89 ( $\alpha$ )	Sq. antiprism	4	2.58
$\text{ThBr}_4$	8	2.85–3.12 ( $\beta$ ); 2.91–3.02 ( $\alpha$ )	Sq. antiprism	4	2.72
$\text{ThI}_4$	8	3.13–3.29	Dodecahedron		



octahedra. However, there is a wide selection of complexes of the smaller fluoride ion, which tend to have higher coordination numbers. The stoichiometry is no guide to the coordination number –  $\text{K}_5\text{ThF}_9$  contains dodecahedral  $[\text{ThF}_8]^{4-}$  ions whilst in  $\text{Li}_3\text{ThF}_7$  and  $(\text{NH}_4)_3\text{ThF}_7$  thorium is nine coordinate

## 10.4 Uranium Halides

These form a large and interesting series of substances, in oxidation states ranging from +3 to +6, illustrating principles of structure and property. The structures of the uranium halides are shown in Figure 10.4.

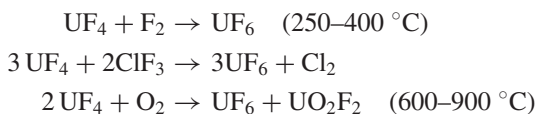
Oxidation state	F	Cl	Br	I
6	$\text{UF}_6$  Octahedron	$\text{UCl}_6$  Octahedron	—	—
5	$\alpha^- \text{UF}_5$ $\beta^-$   Octahedron   Pent-bipy	$\text{UCl}_5$  Oct. dimer	$\text{UBr}_5$  Oct. dimer	—
4	$\text{UF}_4$  Sq. antiprism	$\text{UCl}_4$  Dodecahedron	$\text{UBr}_4$  Pentagonal bipyramid	$\text{UI}_4$  Octahedron (chain)
3	$\text{UF}_3$  Fully capped trigonal prism	$\text{UCl}_3$  Tricapped trigonal prism	$\text{UBr}_3$  Tricapped trigonal prism	$\text{UI}_3$  Bicapped trigonal prism

**Figure 10.4**

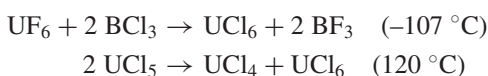
Coordination polyhedra in the uranium halides [adapted from J.C. Taylor, *Coord. Chem. Rev.* 1976, **20**, 203; reprinted with permission of Elsevier Science publishers].

### 10.4.1 Uranium(VI) Compounds

UF<sub>6</sub> and UCl<sub>6</sub> are two remarkable substances, the former on account of its application in isotopic enrichment of uranium (Sections 9.4 and 10.4.5); the latter as the only actinide hexachloride. Colourless UF<sub>6</sub> can be made by a wide variety of routes, including:



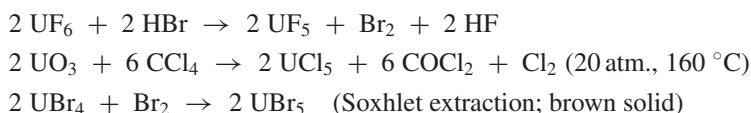
The latter is the Fluorox process, which has the considerable advantage of not requiring the use of elemental fluorine. Dark green, hygroscopic, UCl<sub>6</sub> may be synthesized by halogen exchange or disproportionation:



Both have octahedral molecular structures (U–F = 1.994 Å in UF<sub>6</sub>) and are volatile under reduced pressure at temperatures below 100 °C.

### 10.4.2 Uranium(V) Compounds

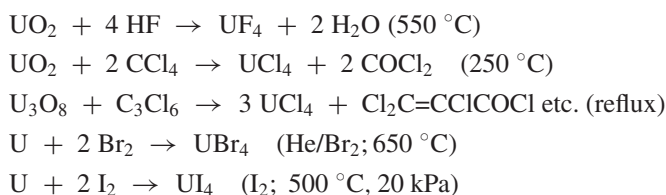
These are among the best characterized compounds in this somewhat rare oxidation state, although they do tend to be unstable (see the preparation of UCl<sub>6</sub>) and UI<sub>5</sub> does not exist.



Grey UF<sub>5</sub> has a polymeric structure with 6- and 7-coordinate uranium, whilst red-brown UCl<sub>5</sub> and brown UBr<sub>5</sub> have a dimeric structure in which two octahedra share an edge.

### 10.4.3 Uranium (IV) Compounds

In normal laboratory work, these are the most important uranium halides, especially UCl<sub>4</sub>.



HF is used in the synthesis of the tetrafluoride since obviously the use of fluorine in this reaction would tend to produce UF<sub>6</sub>. Although Peligot first prepared UCl<sub>4</sub> in 1842 by the reaction of uranium oxide with chlorine and charcoal, nowadays it is conveniently made by refluxing the oxide with organochlorine compounds such as hexachloropropene and CCl<sub>4</sub>. U<sup>4+</sup> does not have reducing tendencies, and UI<sub>4</sub> is stable, though not to hydrolysis.

Table 10.5 lists some properties of these compounds. As usual in the lower oxidation states, the fluorides have significantly lower volatilities. This can alternatively be explained

**Table 10.5** Uranium(IV) halides

	UF <sub>4</sub>	UCl <sub>4</sub>	UBr <sub>4</sub>	UI <sub>4</sub>
Description	Air-stable green solid	Deliquescent green solid	Deliquescent brown solid	Deliquescent black solid
Mp (°C)	1036	590	519	506
Bp (°C)		789	761	
Solubility		H <sub>2</sub> O and most org.solvents	H <sub>2</sub> O and most org.solvents	H <sub>2</sub> O and most org.solvents
Coordination geometry	Square antiprism	Dodecahedron	Pentagonal bipyramid	Octahedron
C.N. of uranium	8	8	7	6
U–X distance (Å)	2.25–2.32	2.64–2.87	2.61 (term.) 2.78–2.95 (bridge)	2.92(term.) 3.08–3.11 (bridge)

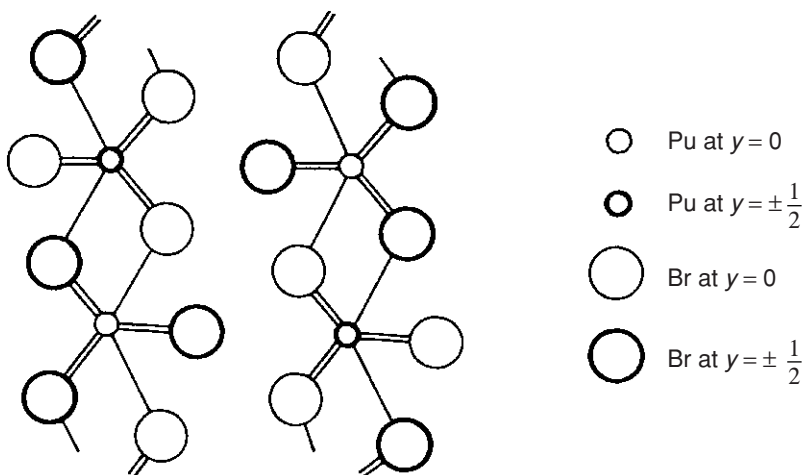
in terms of high lattice energies, on account of the small size of the fluoride ion, or by the greater ionic character in the bonding. In fact, like the other  $\text{MF}_4$  and  $\text{MCl}_4$ ,  $\text{UF}_4$  vapourizes as  $\text{MF}_4$  molecules. As usual, the coordination number C.N. of the metal decreases as the halogen gets larger whilst the bond lengths increase.

#### 10.4.4 Uranium(III) Compounds

Because of the ease of oxidation of the  $\text{U}^{3+}$  ion, these are all made under reducing conditions.



These compounds have structures typical of the actinide trihalides (Section 10.2.2). Green  $\text{UF}_3$  has the 11-coordinate  $\text{LaF}_3$  structure whilst  $\text{UCl}_3$  and  $\text{UBr}_3$ , both red, have the tricapped trigonal prismatic ' $\text{UCl}_3$ ' structure. Nine iodide ions cannot pack round uranium, so black  $\text{UI}_3$  adopts the 8-coordinate  $\text{PuBr}_3$  structure (Figure 10.5).



**Figure 10.5**

The layer structure of  $\text{PuBr}_3$  [after A.F. Wells, *Structural Inorganic Chemistry*, Clarendon Press, Oxford (3rd edn, 1962) and reproduced by permission of the Oxford University Press]. Note that 9-coordination is prevented by non-bonding  $\text{Br} \dots \text{Br}$  interaction. The notation  $y = 0$  and  $y = \pm \frac{1}{2}$  indicates the relative height of atoms with respect to the plane of the paper. The planes of the layers are normal to the plane of the paper.

#### 10.4.5 Uranium Hexafluoride and Isotope Separation

$^{235}\text{U}$  is the only naturally occurring fissionable nucleus, but it makes up only 0.72% of natural uranium. Scientists working on the Manhattan project to build the first atomic bombs in the early 1940s were faced with the problem of producing uranium enriched in  $^{235}\text{U}$ . In principle various routes were available, such as deflection in electric and magnetic fields, diffusion across thermal or osmotic pressure barriers, and ultracentrifugation. E.O. Lawrence developed a modified cyclotron ('calutron') that relied on the fact that  $^{235}\text{UCl}_4^+$

and  $^{238}\text{UCl}_4^+$  ions would follow slightly different paths in a magnetic field and thus be separated. Although eventually gaseous diffusion became the preferred route, the calutron did produce significant amounts of enriched uranium by 1945 that were used to make the first atomic bomb. The preferred technique was eventually gaseous diffusion of  $\text{UF}_6$  through porous membranes, usually of nickel or aluminium, with a pore size ca. 10–25 nm. Graham's law of diffusion indicates that the rate of diffusion of a compound  $\propto \sqrt{1/M_r}$ . A separation factor,  $\alpha^*$ , can be defined as:

$$\alpha^* = \sqrt{M_r(^{238}\text{UF}_6)/M_r(^{235}\text{UF}_6)} = \sqrt{352/349} = 1.00429.$$

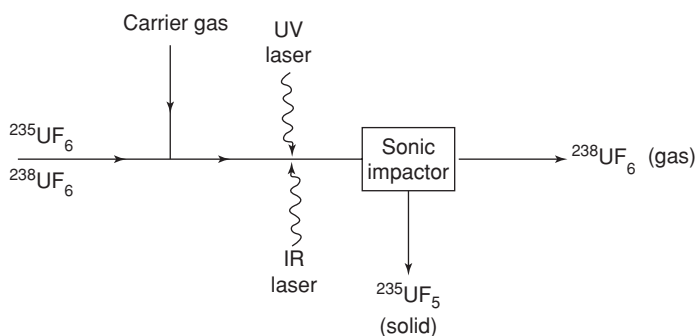
Using a 'cascade' process with up to 3000 stages, an enrichment of up to 90% is obtained.

Desirable qualities for the compound used included high volatility, so that it was easy to convert into a vapour and minimize energy requirements; as low an  $M_r$  as possible, in order to enhance the separation factor; ease of synthesis.  $\text{UF}_6$  met these criteria quite well; in addition, fluorine has only one isotope, so that the  $\text{UF}_6$  molecules of any given uranium isotope all have the same mass and this does not complicate the separation. Although  $\text{UF}_6$  is actually a solid at room temperature and atmospheric pressure, it is by far the most volatile uranium compound (sublimes at 56.5 °C at atmospheric pressure), having a vapour pressure at room temperature of about 120 mm Hg. The principal problem was its high reactivity (many coordination compounds and organometallics were investigated unsuccessfully as possible alternatives). This meant that fluorinated materials had to be developed for valves and lubricants ( $\text{UF}_6$  attacked grease); new pump seals were invented that were gas-tight and greaseless (after the war, the seal material came to be known as Teflon). Fluorine-resistant metals were needed for the porous barriers whilst a high quality of engineering was needed to obtain consistent pore sizes. The process was carried out on a huge scale (acres of pores) so a vast plant was needed and the energy requirements for pumping the vapour were immense.

Other methods have been used to carry out uranium enrichment, again using  $\text{UF}_6$ . Gas centrifuges were developed in the 1960s. On centrifugation, the heavier  $^{238}\text{UF}_6$  molecules are pushed out more by centrifugal force and tend to accumulate in the periphery, with an excess of  $^{235}\text{UF}_6$  in the axial position. Better separations are obtained at lower temperatures and higher speeds. Commercial plants have used series of vacuum tubes containing 2 metre rotors which are spun at 50 000 to 70 000 rpm. Like gaseous diffusion, it runs as a cascade process, but requiring many fewer stages than gaseous diffusion.

Another technique that shows great promise and is still being developed is laser enrichment, which can be applied to either atoms or molecules (Figure 10.6). The molecular laser process exploits the fact that  $^{238}\text{UF}_6$  and  $^{235}\text{UF}_6$  molecules have slightly different vibrational frequencies (of the order of 0.5  $\text{cm}^{-1}$ ). The  $^{235}\text{UF}_6$  molecules in  $\text{UF}_6$  vapour (supercooled in order to produce sharper absorption bands) are selectively excited with a tuneable IR laser, then irradiated with a high-intensity UV laser, whereupon the excited  $^{235}\text{UF}_6$  molecules are photodecomposed into  $^{235}\text{UF}_5$  (the  $^{238}\text{UF}_6$  molecules are unaffected). Under these conditions, the  $^{235}\text{UF}_5$  is a solid, and is separated from the  $^{238}\text{UF}_6$  (using a sonic impactor).

The leading process of this type is the Australian SILEX system (which is also being used to carry out isotopic separation for other elements such as silicon and zirconium).

**Figure 10.6**

Laser separation method for  $^{235}\text{UF}_6$  and  $^{238}\text{UF}_6$  (reproduced with permission from S.A. Cotton, *Lanthanides and Actinides*, Macmillan, 1991, p. 95).

## 10.5 The Actinide Halides (Ac–Am) excluding U and Th

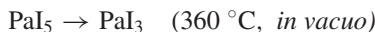
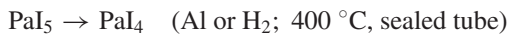
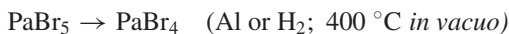
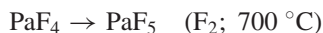
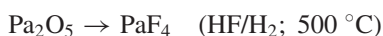
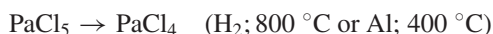
### 10.5.1 Actinium

Actinium forms halides only in the (+3) oxidation state,  $\text{AcX}_3$  and  $\text{AcOX}$  ( $\text{X} = \text{F}, \text{Cl}, \text{Br}$ ). The trihalides have the  $\text{LaF}_3$  ( $\text{X} = \text{F}$ ) and  $\text{UCl}_3$  ( $\text{X} = \text{Cl}, \text{Br}$ ) structures, respectively.

### 10.5.2 Protactinium

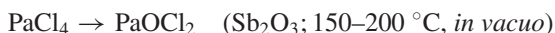
Protactinium has a wealth of halides, with all  $\text{PaX}_4$  and  $\text{PaX}_5$  known, also  $\text{PaI}_3$ . There are also several oxyhalides.

$\text{Pa}_2\text{O}_5$  is the usual starting material for the synthesis of the halides:



Seven coordination is found in both colourless  $\text{PaF}_5$  ( $\beta\text{-UF}_5$  structure) and yellow  $\text{PaCl}_5$  (Figure 10.3; chain structure), whilst two forms of dark red  $\text{PaBr}_5$  adopt the  $\alpha$ - and  $\beta\text{-UCl}_5$  structures, dimeric with six-coordinate protactinium.  $\text{PaX}_4$  ( $\text{X} = \text{F}, \text{Cl}, \text{Br}$ ) have the eight-coordinate  $\text{UF}_4$  ( $\text{X} = \text{F}$ ; square antiprismatic) and  $\text{UCl}_4$  ( $\text{X} = \text{Cl}, \text{Br}$ ; dodecahedral) structures, all eight coordinate; the fluoride is brown, the chloride green-yellow, and the bromide orange-red). Dark brown  $\text{PaI}_3$  is also eight coordinate ( $\text{PuBr}_3$  structure). Protactinium shares the same ability to form oxyhalides as several other

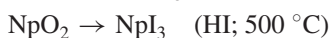
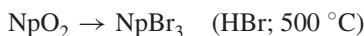
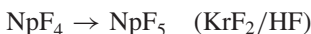
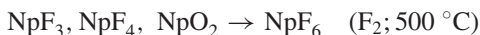
actinides (Ac, Th, U) and transition metals (Nb, Ta, Mo, W).



$\text{PaOBr}_3$  has a cross-linked chain structure with 7-coordinate protactinium, whilst yellow-green  $\text{PaOCl}_2$  has a complicated chain structure involving 7-, 8- and 9- coordination, adopted by several  $\text{MOX}_2$  ( $\text{M} = \text{Th}, \text{Pa}, \text{U}, \text{Np}$ ;  $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ).

### 10.5.3 Neptunium

Neptunium maintains the flavour of a range of halides in different oxidation states, but only fluorides are known in oxidation states above +4. All  $\text{NpX}_3$  are known, with assorted pleasant shades (purple fluoride, green chloride and bromide, brown iodide), together with  $\text{NpX}_4$  ( $\text{X} = \text{F}, \text{Cl}, \text{Br}$ ; green, red-orange, and dark red, respectively),  $\text{NpF}_5$  (blue-white) and  $\text{NpF}_6$  (orange). Attempts to make the plausible  $\text{NpF}_7$  using fluorinating agents like  $\text{NpF}_5$  have not met with success.  $\text{Np}^{\text{IV}}$  has a wide chemistry, but there is no  $\text{NpI}_4$ , though here there are parallels with the inability of iodide to coexist with a stable 'high' oxidation state (*cf.*  $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$  given the instability of the known  $\text{FeI}_3$ ).

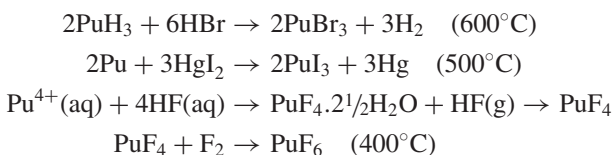


These have the same structures as the uranium analogues, except that a second form of  $\text{NpBr}_3$  has the  $\text{PuBr}_3$  structure. Like  $\text{UF}_6$  and  $\text{PuF}_6$ ,  $\text{NpF}_6$  forms a volatile, toxic vapour (bp  $55.2^\circ\text{C}$ ). Oxyhalides  $\text{NpOF}_3$ ,  $\text{NpO}_2\text{F}_2$ ,  $\text{NpOF}_4$ ,  $\text{NpOCl}$ , and  $\text{NpOI}$  have been described.

### 10.5.4 Plutonium

The tendency towards lower stability of high oxidation state noted with Np is continued here. Though all  $\text{PuX}_3$  exist, pale brown  $\text{PuF}_4$  is the only tetrahalide, and there are no pentahalides, just red-brown  $\text{PuF}_6$ . The trihalides exhibit pastel colours (fluoride violet-blue; chloride blue-green; bromide light green; iodide bright green). The (+2) state is not accessible; with the next actinide, americium, the reaction with mercury(II) iodide yields  $\text{AmI}_2$ .





Two further points merit attention.  $\text{PuF}_6$  is a very volatile substance, like the other actinide hexafluorides (mp  $51.5^\circ\text{C}$ ; bp  $62.15^\circ\text{C}$ ); very reactive (it undergoes controlled hydrolysis to  $\text{PuO}_2\text{F}_2$  and  $\text{PuOF}_4$ ), it tends to be decomposed by its own  $\alpha$ -radiation, and is best kept in the gaseous state (resembling  $\text{NO}_2$  in appearance).

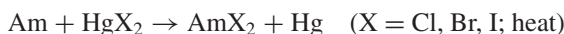
As already noted,  $\text{PuCl}_4$  does not exist in the solid state; however, it has been detected in the gas phase above  $900^\circ\text{C}$  by its UV–visible absorption spectrum, so the equilibrium below moves to the right on heating:



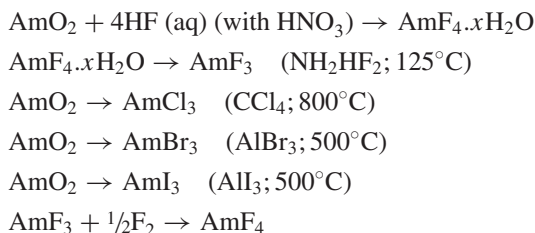
Halide complexes in the (+4) state are stable for all but iodides. Apart from the two mentioned above, other oxyhalides include  $\text{PuO}_2\text{Cl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{PuOX}$  ( $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$ ), the absence of any in the (+4) and (+5) states is again notable.

### 10.5.5 Americium

At americium, dihalides become isolable for the first time.



They are black solids with the  $\text{PbCl}_2$  ( $\text{X} = \text{Cl}$ );  $\text{EuBr}_2$  ( $\text{X} = \text{Br}$ ); and  $\text{EuI}_2$  ( $\text{X} = \text{I}$ ) structures. As with plutonium, only fluorides occur in the higher ( $>3$ ) oxidation states. The trihalides are important; they have the usual pastel colours, pink in the case of the fluoride and chloride, white–pale yellow (bromide), and pale yellow (iodide).



There is an unsubstantiated report of the isolation of  $\text{AmF}_6$  (Iu. V. Drobyshevshii *et al.*, *Radiokhimiya*, 1980, **22**, 591):



The product was a volatile dark brown solid, with an IR absorption at  $604\text{ cm}^{-1}$  (compare  $\nu\text{ U–F}$  at  $624\text{ cm}^{-1}$  in  $\text{UF}_6$ ).



## 10.6 Halides of the Heavier Transactinides

Earlier mention (Section 10.2.2 and Tables 10.1–10.3) of the trihalides of the transplutonium elements does not do justice to the synthetic expertise of experimentalists who have studied these compounds. Some examples of the techniques involved follow.

### 10.6.1 Curium(III) Chloride

The first synthesis, reported in the mid 1960s, was made difficult by the use of the short-lived  $^{244}\text{Cm}$  ( $t_{1/2} = 18.1$  y) isotope, which caused significant damage to the sample through irradiation. However, by 1970 microgram quantities of  $^{248}\text{Cm}$  ( $t_{1/2} = 3.4 \times 10^5$  y) were available, albeit on a microgram scale. Ion-exchange beads were loaded with  $1\ \mu\text{g}$  of  $^{248}\text{Cm}$ , then heated to  $1200\ ^\circ\text{C}$  to convert the curium into the oxide; the  $\text{Cm}_2\text{O}_3$  was placed in capillaries and chlorinated using  $\text{HCl}$  at  $500\ ^\circ\text{C}$ , forming pale yellow  $\text{CmCl}_3$ . Slow cooling of molten  $\text{CmCl}_3$  from over  $600\ ^\circ\text{C}$  afforded a single crystal of the curium chloride, which when studied by X-ray diffraction revealed its adoption of the  $\text{UCl}_3$  structure and afforded the  $\text{Cm}-\text{Cl}$  bond lengths (J. R. Peterson and J. H. Burns, *J. Inorg. Nucl. Chem.*, 1973, **35**, 1525).

### 10.6.2 Californium(III) Chloride, Californium(III) Iodide, and Californium(II) Iodide

$\text{CfCl}_3$  was first reported by Burns *et al.*, in 1973, synthesized by the ion-exchange bead route described above. As more  $^{249}\text{Cf}$  ( $t_{1/2} = 351$  y) became available on the  $\mu\text{g}$  scale, another route was employed. A precipitate of californium oxalate was filtered in a quartz capillary using a piece of ashless filter paper. Heating at  $800\text{--}900\ ^\circ\text{C}$  destroyed the filter paper and turned the oxalate into  $\text{Cf}_2\text{O}_3$ , which reacted with  $\text{CCl}_4$  at  $520\text{--}550\ ^\circ\text{C}$  to form lime-green  $\text{CfCl}_3$ . X-ray diffraction showed that this had the  $\text{UCl}_3$  structure. The  $\text{CfCl}_3$  was purified by sublimation at  $800\ ^\circ\text{C}$ , then employed in the synthesis of two iodides:



The yellow-orange triiodide forms the lavender-violet diiodide on reduction:



These compounds were identified using X-ray diffraction and UV-visible spectroscopy.

### 10.6.3 Einsteinium(III) Chloride

The first synthesis of this compound was carried out on the nanogram scale in 1968 by Peterson's group in the face of several difficulties. The  $^{253}\text{Es}$  isotope is so short lived ( $t_{1/2} = 20$  d) that it releases some  $1400\ \text{kJ mol}^{-1}\ \text{min}^{-1}$ , sufficient to dislocate the crystal lattice within 3 minutes of formation and it is also capable of destroying ion-exchange resins. Around 200 nanograms of einsteinium were absorbed by a charcoal chip, which was heated to turn the Es into  $\text{Es}_2\text{O}_3$ , then chlorinated using  $\text{CCl}_4$  to form  $\text{EsCl}_3$ . A crystal of  $\text{EsCl}_3$  was just heated to below its melting point, so that defects in the lattice produced by the radiation were continuously annealed out. One decade later, in 1978, a different route was employed by Peterson to make  $\text{Es}_2\text{O}_3$ , first precipitating the oxalate, then converting it into the oxide by calcination. Treatment of the oxide first with  $\text{HF}$ , then fluorine at  $300\ ^\circ\text{C}$ ,

yielded the fluoride EsF<sub>3</sub>. The absorption spectrum of EsF<sub>3</sub> was examined over a period of 2 years, so that additionally the spectra of the <sup>249</sup>BkF<sub>3</sub> daughter and <sup>249</sup>CfF<sub>3</sub> granddaughter were also obtained, enabling their assignment of the LaF<sub>3</sub> structure.

10.7 Oxides

Table 10.6 summarizes the formulae of the oxides. It should be emphasized that this represents a simplification and, especially for U and Pu, a number of phases exist between the compositions shown.

The pattern of oxidation state here is very different to that of the lanthanides, where the common oxides are Ln<sub>2</sub>O<sub>3</sub>. The early actinides in particular show much more resemblance to the transition metals, where the maximum oxidation state corresponds to the number of ‘outer shell’ electrons; this reflects the greater availability of d and f electrons in the actinide elements. The +4 state in particular is more stable than in the lanthanide series, where it is only encountered in a few ions.

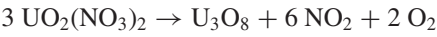
10.7.1 Thorium Oxide

ThO<sub>2</sub>, is a white solid that adopts the fluorite structure (as do the MO<sub>2</sub> phases of the other actinides). When heated it gives off a rather bluish light; if about 1% cerium is added, the light is both whiter and more intense so that the mixture came to be used in making incandescent gas mantles, widely used for lighting until comparatively recently.

10.7.2 Uranium Oxides

The uranium–oxygen phase diagram is very complicated, with some of the 14 reported phases not being genuine and several phases showing variable composition. The important phases are UO<sub>2</sub>, U<sub>4</sub>O<sub>9</sub>, U<sub>3</sub>O<sub>8</sub>, and UO<sub>3</sub>. Brown-black UO<sub>2</sub> has the fluorite structure. It is best made by reduction of higher uranium oxides (e.g. UO<sub>3</sub> with H<sub>2</sub> or CO at 300–600 °C).

Additional oxygen can be incorporated into interstitial sites in the basic fluorite structure until the composition reaches U<sub>4</sub>O<sub>9</sub>(black UO<sub>2.25</sub>). Green-black U<sub>3</sub>O<sub>8</sub> is the result of heating uranyl salts at around 650–800 °C; above 800 °C, it tends to lose oxygen.



This is a mixed-valence compound with pentagonal bipyramidal coordination of uranium. Addition of more oxygen eventually results in orange-yellow UO<sub>3</sub>. This has several crystalline forms, most of which contain uranyl groups in 2 + 4 coordination, and can be made by heating, e.g., (NH<sub>4</sub>)<sub>2</sub>U<sub>2</sub>O<sub>7</sub> or UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> at 400–600 °C (above which temperature, oxygen loss to U<sub>3</sub>O<sub>8</sub> tends to occur). When uranium oxides are heated with M<sub>2</sub>CO<sub>3</sub> or M’CO<sub>3</sub>

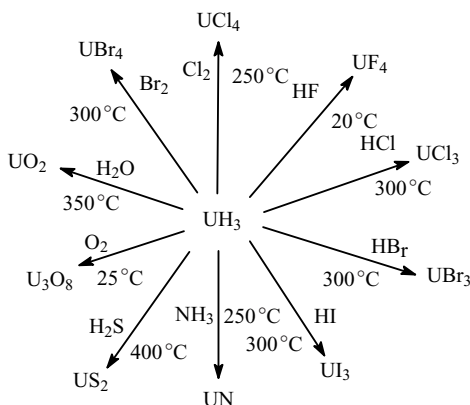
Table 10.6 Oxides of the actinide elements

Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es
Ac <sub>2</sub> O <sub>3</sub>	ThO <sub>2</sub>	Pa <sub>2</sub> O <sub>5</sub>	UO <sub>2</sub>	NpO <sub>2</sub>	Pu <sub>2</sub> O <sub>3</sub>	Am <sub>2</sub> O <sub>3</sub>	Cm <sub>2</sub> O <sub>3</sub>	Bk <sub>2</sub> O <sub>3</sub>	Cf <sub>2</sub> O <sub>3</sub>	Es <sub>2</sub> O <sub>3</sub>
			UO <sub>3</sub>	Np <sub>2</sub> O <sub>5</sub>	PuO <sub>2</sub>	AmO <sub>2</sub>	CmO <sub>2</sub>	BkO <sub>2</sub>	CfO <sub>2</sub>	
				NpO <sub>3</sub> (?)						

(M, M' are group I or II metals), uranates with formulae such as  $\text{Na}_2\text{UO}_4$  or  $\text{K}_2\text{U}_2\text{O}_7$  result; unlike d-block metal compounds with similar formulae, these contain  $\text{UO}_6$  polyhedra.

## 10.8 Uranium Hydride $\text{UH}_3$

The +3 oxidation state of uranium is strongly reducing, so it is not altogether surprising to find it forms a stable hydride. Massive uranium reacts with hydrogen gas on heating to around  $250^\circ\text{C}$  (at lower temperatures if powdered metal is used), swelling up to a fine black powder, which is pyrophoric in air. It decomposes on further heating ( $350\text{--}400^\circ\text{C}$  under a hydrogen atmosphere) to hydrogen and uranium powder, so that making then decomposing the hydride can be a useful way of preparing a reactive form of the metal (a strategy that can be followed with other actinides, e.g. Th). Some reactions of  $\text{UH}_3$  are summarized in Figure 10.7. The crystal structure shows that each uranium has 12 hydrogen neighbours.

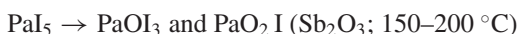
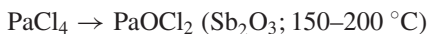


**Figure 10.7**  
Reactions of  $\text{UH}_3$ .

## 10.9 Oxyhalides

Although not binary compounds, a discussion of actinide oxyhalides is not out of place here. A number of these are formed by the earlier actinides, another difference between the 4f and 5f metals.

Thorium forms  $\text{ThOX}_2$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) but there is a greater variety with protactinium:

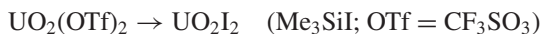
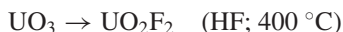


Of these, yellow  $\text{PaOBr}_3$  has a cross-linked chain structure with seven-coordinate Pa (bound to 3 O and 4 Br). Yellow-green  $\text{PaOCl}_2$  has an important structure adopted by many

oxyhalides  $\text{MOX}_2$  ( $X = \text{Cl, Br, I}$ ;  $M = \text{Th, Pa, U, Np}$ ), which contains seven-, eight-, and nine-coordinate Pa.

Neptunium forms  $\text{NpOF}_3$ ,  $\text{NpO}_2\text{F}_2$ ,  $\text{NpOF}_4$ , and  $\text{NpOX}$  ( $X = \text{Cl, I}$ ), whilst the plutonium compounds  $\text{PuOX}$  ( $X = \text{F, Cl, Br, I}$ ),  $\text{PuO}_2\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{PuOF}_4$ , and  $\text{PuO}_2\text{F}_2$  are known, as well as  $\text{AmO}_2\text{F}_2$  (and certain americium oxychloride complexes).

The most important oxyhalides, though, are the uranium compounds. Yellow  $\text{UO}_2\text{F}_2$  and  $\text{UO}_2\text{Cl}_2$ , and red  $\text{UO}_2\text{Br}_2$ , have been known for a long while, but the existence of beige  $\text{UO}_2\text{I}_2$  was doubted for many years, only being confirmed very recently (2004) by Berthet *et al.*



In the solid state,  $\text{UO}_2\text{F}_2$  has a structure in which a uranyl unit is bound to six fluorides (all bridging); whilst in  $\text{UO}_2\text{Cl}_2$  uranium is bound to the two 'oxo' oxygens, four chlorines, and another oxygen, from another uranyl unit.  $\text{UO}_2\text{I}_2$  has not been obtained in crystalline form, but it is soluble in pyridine and THF (L), forming  $\text{UO}_2\text{I}_2\text{L}_3$ , which have pentagonal bipyramidal coordination of uranium, with the usual *trans*-  $\text{O}=\text{U}=\text{O}$  linkage.

A number of adducts of the oxyhalides are well characterized, such as *all-trans*- $[\text{UO}_2\text{X}_2\text{L}_2]$  [ $X = \text{Cl}$ ,  $L = \text{Ph}_3\text{PO}$ ;  $X = \text{Br}$ ,  $L = (\text{Me}_2\text{N})_3\text{PO}$ ;  $X = \text{I}$ ,  $L = (\text{Me}_2\text{N})_3\text{PO}$ ,  $\text{Ph}_3\text{PO}$ ,  $\text{Ph}_3\text{AsO}$ ]. Others are anionic, containing ions such as  $[\text{UO}_2\text{F}_5]^{3-}$  and  $[\text{UO}_2\text{X}_4]^{2-}$  ( $X = \text{Cl, Br}$ ). Hydrates have recently been reported of the bromide and iodide, *all-trans*- $\text{UO}_2\text{I}_2(\text{OH}_2)_2 \cdot 4\text{Et}_2\text{O}$ ,  $[\text{UO}_2\text{Br}_2(\text{OH}_2)_3]$  (*cis*-equatorial bromides), and the dimer  $[\text{UO}_2\text{Br}_2(\text{OH}_2)_2]_2$ , which is  $[\text{Br}(\text{H}_2\text{O})_2\text{O}_2\text{U}(\mu\text{-Br})_2\text{UO}_2\text{Br}(\text{OH}_2)_2]$ .

**Question 10.1** Discuss the halides formed by the actinides, commenting on the trends in oxidation state as the series is crossed.

**Answer 10.1** Early on in the series, as far as uranium, the maximum oxidation state corresponds to the total number of 'outer shell' electrons. Uranium forms a hexachloride, in addition to the  $\text{MF}_6$  also formed by Np and Pu. After uranium, neptunium forms the full range of tetrahalides, but, from plutonium onwards, the (+3) state dominates the chemistry of the binary halides, which strongly resemble those of the lanthanides. This may reflect decreased availability of 5f (and 6d?) electrons for bonding. As usual, F supports the highest oxidation states.

**Question 10.2** Study the information about the thorium tetrahalides in Table 10.4 and comment on the trends and patterns in it.

**Answer 10.2** The bond lengths increase as the atomic number of the halogen increases, since the atomic (ionic) radius of the halogen increases. The bond length is less for the  $\text{ThX}_4$  molecules in the gas phase than for the corresponding 8-coordinate species in the solid state; again this is expected since there will be more interatomic repulsion in the eight-coordinate species. Since there is no obvious pattern in which compounds adopt particular polyhedra in

the solid state, this suggests that the dodecahedron and square antiprism have very similar energies. [It may be parenthetically noted that there is no decrease in coordination number as the size of the halogen increases, as seen for uranium (Figure 10.4).]

**Table 10.7** Melting points and boiling points of uranium chlorides

	UCl <sub>3</sub>	UCl <sub>4</sub>	UCl <sub>5</sub>	UCl <sub>6</sub>
Mp (°C)	835	590	287	177.5 (dec.)
Bp (°C)	dec.	790		

**Question 10.3** Table 10.7 shows the melting and boiling points of the chlorides of uranium. Comment on how these relates to their structures.

**Answer 10.3** There is a clear relationship with the degree of molecularity. UCl<sub>6</sub> has a monomeric molecular structure with relatively weak intermolecular forces and is therefore the most volatile (and on account of its high oxidation state, the least stable); UCl<sub>5</sub> is dimeric U<sub>2</sub>Cl<sub>10</sub>, therefore as a larger molecule will have stronger intermolecular forces and be less volatile than UCl<sub>6</sub>. Continuing to UCl<sub>4</sub> and UCl<sub>3</sub>, the more halogens surrounding the uranium, the more energy will be needed to break the lattice into small mobile units, and the higher will be the melting and boiling points.

**Question 10.4** Thorium(IV) oxide has a melting point of 3390 °C. Explain why.

**Answer 10.4** It is composed of Th<sup>4+</sup> and O<sup>2-</sup> ions. The strong electrostatic attraction between these highly charged ions (a very high lattice energy) means that a great deal of energy has to be supplied to overcome the attraction in order to free the ions and melt it.

**Question 10.5** Write equations for the reduction of UO<sub>3</sub> by both hydrogen and carbon monoxide.

**Answer 10.5**  $\text{UO}_3 + \text{H}_2 \rightarrow \text{UO}_2 + \text{H}_2\text{O}$ ;  $\text{UO}_3 + \text{CO} \rightarrow \text{UO}_2 + \text{CO}_2$

**Question 10.6** UH<sub>3</sub> is high melting and has a high conductivity, similar to uranium metal. Comment on its bonding and structure.

**Answer 10.6** The high conductivity suggests the presence of delocalized electrons. One possible structure is U<sup>4+</sup>(H<sup>-</sup>)<sub>3</sub>(e<sup>-</sup>); the ionic nature would explain the high melting point.

# 11 Coordination Chemistry of the Actinides

By the end of this chapter you should be able to:

- recognize +4 and +6 as the main oxidation states for uranium and +4 as the only important oxidation state for thorium;
- appreciate that coordination numbers of  $>6$  are the norm;
- be familiar with the main features of the chemistry of the other actinides, and appreciate the transition in chemical behaviour across the series;
- appreciate the importance of nitrate complexes;
- recognize the characteristic structures of uranyl complexes;
- suggest structures for compounds;
- explain the separation of nuclear material and the recovery of U and Pu in terms of the chemistry involved;
- appreciate the problems presented in nuclear waste disposal and understand the solutions;
- suggest safe ways to handle actinide compounds.

## 11.1 Introduction

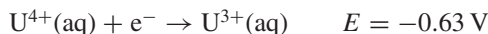
Studies of the coordination chemistry of the actinides have been limited by a number of factors – the care needed in handling radioactive materials and the possibility of damage to human tissue from the radiation; toxicity (especially Pu); the very small quantities available and very short half-lives of the later actinides; radiation and heating damage to solutions; and radiation damage (defects and dislocations) to crystals.

The vast majority of the studies reported have concerned the metals thorium and uranium, particularly the latter, due to accessibility of raw materials, ease of handling, and the long lifetimes of the relatively weakly  $\alpha$ -emitting elements Th and U. In many cases, compounds of neptunium and plutonium with similar formulae to U and Th analogues have been made and found to be isomorphous and thus presumably isostructural. This chapter will therefore commence with, and concentrate largely on, the chemistry of complexes of these elements, followed by sections on the other actinides.

## 11.2 General Patterns in the Coordination Chemistry of the Actinides

As noted earlier (Table 9.2), the patterns of oxidation states of the early actinides resemble those of d-block metals, with the maximum oxidation state corresponding to the number of ‘outer shell’ electrons. Thus the chemistry of thorium is essentially confined to the +4

state (to an even greater degree than Zr or Hf) but uranium exhibits oxidation states of +3, +4, +5, and +6, with most compounds being in either the +4 or +6 state. The reason for this is that uranium(III) compounds tend to be easy to oxidize:



whilst under aqueous conditions the  $\text{UO}_2^+$  ion readily disproportionates to a mixture of  $\text{U}^{4+}$  and  $\text{UO}_2^{2+}$  [though there is a chemistry of uranium(V) in non-aqueous solvents].

As the actinide series is crossed, it becomes harder to involve the f electrons in compound formation, so that the later actinides increasingly show a chemistry in the +3 state, resembling the lanthanides, but with a more prominent +2 state.

### 11.3 Coordination Numbers in Actinide Complexes

As for the lanthanides, actinide complexes display high coordination numbers. A study of the aqua ions of early actinides makes an interesting comparison (Table 11.1 lists numbers of water molecules and bond lengths).

**Table 11.1** Actinide aqua ions – numbers of bound water molecules and metal–water distances<sup>a</sup>

Ox state		Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf
6	$\text{MO}_2^{2+}$				5.0	5.0	6.0				
	M–OH <sub>2</sub> (Å)				2.40	2.42	2.40–2.45				
5	$\text{MO}_2^+$					5.0	4.0				
	M–OH <sub>2</sub> (Å)					2.50	2.47				
4	$\text{M}^{4+}$		10.0		9.0; 10.0	11.2	8 or 9				
	M–OH <sub>2</sub> (Å)		2.45		2.51; 2.42	2.40	2.39				
3	$\text{M}^{3+}$				9 or 10	9 or 10	10.2	10.3	10.2		8.5 ± 1.5
	M–OH <sub>2</sub> (Å)				2.61	2.52	2.51	2.48	2.45		2.4

<sup>a</sup> The uncertainty in the hydration number is generally in the region of 1.

The best characterized aqua ion is the hydrated uranyl ion  $[\text{UO}_2(\text{OH}_2)_5]^{2+}$ , which has been isolated in several salts studied by diffraction methods as well as X-ray absorption methods (EXAFS) in solution. However, similar ions are firmly believed to exist in the cases of  $[\text{MO}_2(\text{aq})]^{2+}$  (M = Np, Pu) and  $[\text{MO}_2(\text{aq})]^+$  (M = U, Np, Pu). In studying Table 11.1, two features stand out. Ions like  $\text{UO}_2^{2+}$  are unprecedented in lanthanide chemistry, both in respect of the +6 oxidation state and also in the presence of strong and non-labile U=O bonds. Secondly, the coordination numbers of the hydrated +3 actinide ions appear to be higher than those of the  $\text{Ln}^{3+}$  ions (9 for early lanthanides, 8 for later ones), explicable on account of the slightly higher ionic radii of the actinide ions. One of the few other characterized aqua ions is the trigonal prismatic  $[\text{Pu}(\text{H}_2\text{O})_9]^{3+}$ , strongly resembling the corresponding lanthanide series.

### 11.4 Types of Complex Formed

Table 11.2 gives some stability constants for complexes of  $\text{Th}^{4+}$  and  $\text{UO}_2^{2+}$ . Thorium forms stronger complexes with fluoride, the ‘hardest’ halide ion, than with chloride and bromide; this is the behaviour expected of a ‘hard’ Lewis acid. Thorium also forms quite

**Table 11.2** Stability constants of  $\text{Th}^{4+}$  and  $\text{UO}_2^{2+}$  complexes

Stability constants for complexes of $\text{Th}^{4+}$						Stability constants for complexes of $\text{UO}_2^{2+}$		
Ligand	$I$ (mol/dm <sup>3</sup> )	Log $K_1$	Log $K_2$	Log $K_3$	Log $K_4$	Ligand	$I$ (mol/dm <sup>3</sup> )	Log $K_1$
$\text{F}^-$	0.5	7.56	5.72	4.42		$\text{F}^-$	1	4.54
	1	7.46				$\text{Cl}^-$	1	−0.10
$\text{Cl}^-$	1	0.18				$\text{Br}^-$	1	−0.3
$\text{Br}^-$	1	−0.13				$\text{NO}_3^-$	1	−0.3
$\text{NO}_3^-$	1	0.67				$\text{EDTA}^{4-}$	0.1	7.4
$\text{SO}_4^{2-}$	2	3.3	2.42					
$\text{NCS}^-$	1	1.08						
$\text{EDTA}^{4-}$	0.1	25.3						
$\text{acac}^-$	0.1	8.0	7.5	6.0	5.3			

strong complexes with oxygen-donor ligands like nitrate. The hexadentate ligand  $\text{EDTA}^{4-}$  forms very stable complexes, due largely to the favourable entropy change when six water molecules are replaced.

## 11.5 Uranium and Thorium Chemistry

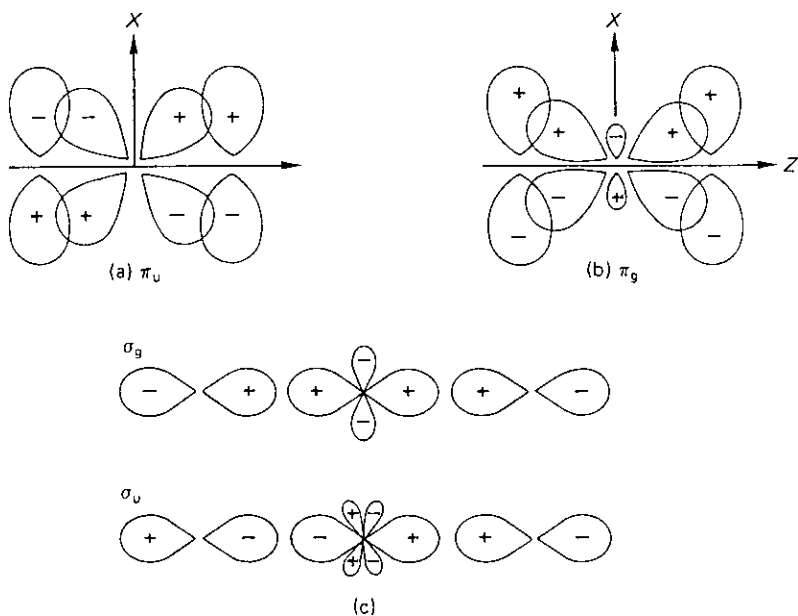
### 11.5.1 Uranyl Complexes

The great majority of uranium(VI) compounds contain the  $\text{UO}_2$  group and are known as uranyl compounds; exceptions are a few molecular compounds, such as the halides  $\text{UOF}_4$ ,  $\text{UF}_6$ , and  $\text{UCl}_6$ , and some alkoxides such as  $\text{U(OMe)}_6$ . Uranyl compounds result eventually from exposure of compounds of uranium in other oxidation states to air. They characteristically have a yellow fluorescence under UV light; from the early 19th century, glass manufacturers added uranium oxide when making yellow and green glass (it is sometimes known as Vaseline glass).

Uranyl complexes can be thought of as derivatives of the  $\text{UO}_2^{2+}$  ion. There is a very wide range of them; they may be cationic, such as  $[\text{UO}_2(\text{OH}_2)_5]^{2+}$  ions; neutral, e.g.  $[\text{UO}_2(\text{OPPh}_3)_2\text{Cl}_2]$ ; or anionic, such as  $[\text{UO}_2\text{Cl}_4]^{2-}$ , yet all feature a *trans*- $\text{UO}_2$  grouping with the characteristic short U–O bonds (1.7–1.9 Å), quite comparable with those found in ‘osmyl’ compounds, which have the  $\text{OsO}_2$  grouping. The presence of the uranyl group can readily be detected in the IR spectrum of a uranium compound through the presence of a strong band in the region 920–980  $\text{cm}^{-1}$  caused by the asymmetric O–U–O stretching vibration; a corresponding band around 860  $\text{cm}^{-1}$  caused by the symmetric O–U–O stretching vibration is seen in the Raman spectrum. Fine structure due to symmetric uranyl stretching vibrations can be seen on an absorption peak in the spectrum of uranyl complexes around 450 nm (Figure 12.1). There has been considerable speculation on the bonding in the uranyl ion. The essentially linear geometry of the  $\text{UO}_2$  unit is an invariable feature of uranyl complexes; no other atoms can approach the uranium nearer than  $\sim 2.2$  Å. Uranium d–p and f–p  $\pi$  bonding have both been invoked to explain the bonding (Figure 11.1).

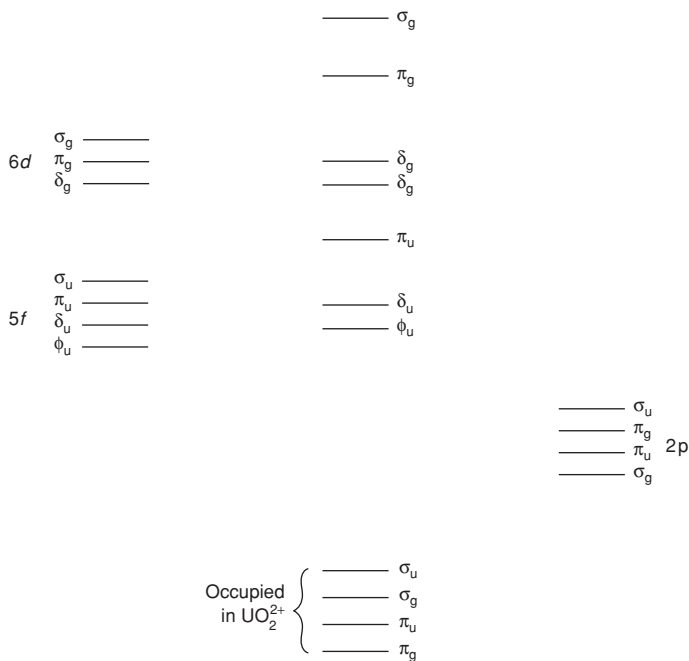
An energy level diagram for the uranyl ion is shown in Figure 11.2. An electron count takes 6 electrons from uranium, four from each oxygen, deducting two for the positive charges; alternatively, if the uranyl ion is thought of as a combination of  $\text{U}^{6+}$  and two  $\text{O}^{2-}$ , taking six electrons from each oxide and none from  $\text{U}^{6+}$ , again giving 12. These completely occupy the six  $\sigma_u$ ,  $\sigma_g$ ,  $\pi_u$ , and  $\pi_g$  molecular orbitals ( $\sigma_u^2 \sigma_g^2 \pi_u^4 \pi_g^4$ ). It has been suggested





**Figure 11.1**

$\pi$ -bonding in the uranyl,  $[\text{UO}_2]^{2+}$  ion: (a)  $d_{xz}$ - $p_x$  overlap; (b)  $f_{xz^2}$ - $p_x$  overlap; (c)  $\sigma$ -bonding in the uranyl ion (reproduced with permission from Figure 3.24 of S.A. Cotton, *Lanthanides and Actinides*, Macmillan, 1991).



The relative ordering of the bonding MOs is uncertain

**Figure 11.2**

M.O. scheme for the uranyl ion,  $\text{UO}_2^{2+}$  (reproduced with permission from Figure 3.25 of S.A. Cotton, *Lanthanides and Actinides*, Macmillan, 1991).

that repulsion (antibonding overlap) between oxygen p orbitals and occupied uranium 6d and 5f orbitals may destabilize the bonding d molecular orbitals, causing them to be higher in energy than the  $\pi$  bonding orbitals, as shown. Addition of further electrons puts them in the essentially non-bonding  $\delta_u$  and  $\phi_u$  orbitals, accounting for the existence of the rather less stable  $\text{MO}_2^{2+}$  (M = Np, Pu, Am) ions.

The uranium(V) species  $\text{UO}_2^+$  exists, but is less stable than  $\text{UO}_2^{2+}$ , possibly owing to weaker overlap; it readily decomposes by disproportionation:



In contrast to the *trans* geometry of  $\text{UO}_2^{2+}$ , isoelectronic ( $6d^0 5f^0$ )  $\text{ThO}_2$  molecules in the gas phase or in low temperature matrices are bent ( $\angle\text{O}-\text{Th}-\text{O} \sim 122^\circ$ ); this is thought to be due to the thorium 5f orbitals being much higher in energy (in uranium, the 5f orbitals are well below 6d), reducing possibilities of 5f–p overlap, so that thorium resorts to using 6d orbitals in the p bonding, like transition metals, as in the case of  $\text{MoO}_2^{2+}(5d^0)$  and  $\text{WO}_2^{2+}(6d^0)$  ions which also adopt bent, *cis* geometries ( $\angle\text{O}-\text{M}-\text{O} \sim 110^\circ$ ).

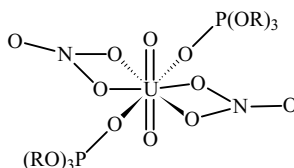
### 11.5.2 Coordination Numbers and Geometries in Uranyl Complexes

An extensive range of uranyl complexes has been prepared and had their structures determined. Their structure can be summarized as a uranyl ion surrounded by a ‘girdle’ of 4, 5, or 6 donor atoms round its waist (a rare example of 2 + 3 coordination is known for a complex of the uranyl ion with a calixarene ligand; another is the amide complex  $[\text{K}(\text{thf})_2][\text{UO}_2\{\text{N}(\text{SiMe}_3)_2\}_3]$ ). If the ligands are monodentate donors, there are usually 4 of them, unless they are small, like F or NCS, when five can be accommodated. When bidentate ligands with small steric demands like  $\text{NO}_3$ ,  $\text{CH}_3\text{COO}$ , and  $\text{CO}_3$  can be accommodated, six donor atoms can surround the uranyl group. In general if there are 4 or 5 donor atoms round the waist, they are reasonably coplanar, but puckering sometimes occurs when there are six. Table 11.3 shows examples of uranium complexes for 5-, 6-, 7-, and 8-coordination.

**Table 11.3** Uranyl complexes

5-coordinate (2 + 3)	6-coordinate (2 + 4)	7-coordinate (2 + 5)	8-coordinate (2 + 6)
$[\text{UO}_2\{\text{N}(\text{SiMe}_3)_2\}_3]^-$	$\text{Cs}_2[\text{UO}_2\text{Cl}_4]$ $(\text{Me}_4\text{N})_2[\text{UO}_2\text{Br}_4]$ $\text{MgUO}_4$ $\text{BaUO}_4$	$\text{UO}_2\text{Cl}_2$ $\text{UO}_2(\text{superphthalocyanine})$ $[\text{UO}_2(\text{NO}_3)_2(\text{Ph}_3\text{PO})]$ $[\text{UO}_2(\text{L})_5]^{2+}$ (L, e.g., $\text{H}_2\text{O}$ , DMSO, urea)	$\text{UO}_2\text{F}_2$ $\text{UO}_2\text{CO}_3$ $[\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2]$ $\text{CaUO}_4$ $\text{SrUO}_4$ $\text{Rb}[\text{UO}_2(\text{NO}_3)_3]$

The uranium(VI) aqua ion is now firmly established as the pentagonal bipyramidal  $[\text{UO}_2(\text{OH}_2)_5]^{2+}$ ; it has been found in crystals of the salt  $[\text{UO}_2(\text{OH}_2)_5](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$  ( $\text{U}=\text{O}$  1.702 Å,  $\text{U}-\text{OH}_2$  2.421 Å) and also found in solutions by X-ray diffraction studies. Similar  $[\text{UO}_2(\text{L})_5]^{2+}$  ions (L = urea,  $\text{Me}_2\text{SO}$ ,  $\text{HCONMe}_2$ ) also exist. Uranyl nitrate forms complexes with phosphine oxides of the type  $[\text{UO}_2(\text{NO}_3)_2(\text{R}_3\text{PO})_2]$ ; similar phosphate complexes  $[\text{UO}_2(\text{NO}_3)_2\{(\text{RO})_3\text{PO}\}_2]$  are important in the extraction of uranium in nuclear waste processing (Figure 11.3 and Section 11.5.5). A number of structures of these complexes are known; for example, when  $\text{R}=\text{isobutyl}$ ,  $\text{U}=\text{O}$  1.757 Å;  $\text{U}-\text{O}(\text{P})$  2.372 Å;  $\text{U}-\text{O}(\text{N})$  2.509 Å.

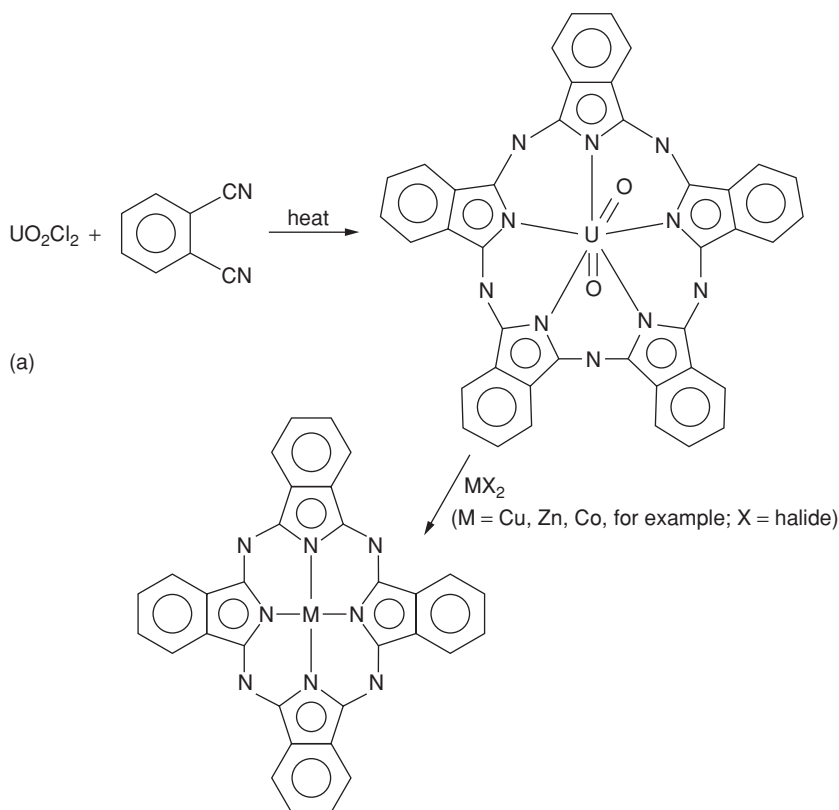


**Figure 11.3**  
Structure of  $\text{UO}_2(\text{NO}_3)_2[(\text{RO})_3\text{PO}]_2$ .

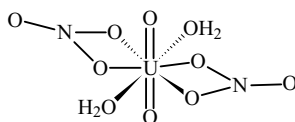
### 11.5.3 Some Other Complexes

Uranyl carbonate complexes have attracted considerable interest in recent years as they are intermediates in the processing of mixed oxide reactor fuels and in extraction of uranium from certain ores using carbonate leaching; more typically they can be formed when uranyl ores react with carbonate or bicarbonate ions underground, and can be present in relatively high amounts in groundwaters. The main complex formed in carbonate leaching of uranyl ores is 8 coordinate  $[\text{UO}_2(\text{CO}_3)_3]^{3-}$ , but around pH 6 a cyclic trimer  $[(\text{UO}_2)_3(\text{CO}_3)_6]^{6-}$  has been identified.

$\text{UO}_3$  dissolves in acetic acid to form yellow uranyl acetate,  $\text{UO}_2(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ . It formerly found use in analysis since, in the presence of  $\text{M}^{2+}$  ( $\text{M} = \text{Mg}$  or  $\text{Zn}$ ), it precipitates sodium ions as  $\text{NaM} [\text{UO}_2(\text{CH}_3\text{COO})_3]_3 \cdot 6\text{H}_2\text{O}$ .



**Figure 11.4**  
Structure and reaction of “uranyl superphthalocyanine”.



**Figure 11.5**  
Structure of  $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2$ .

Uranyl chloride,  $\text{UO}_2\text{Cl}_2$ , reacts on heating with *o*-phthalodinitrile to form a so-called ‘superphthalocyanine’ complex with 2 + 5 coordination (Figure 11.4); other metals (lanthanides, Co, Ni, Cu) react with this, forming a conventional phthalocyanine, so that the uranyl ion has an important role in sustaining this unusual structure.

### 11.5.4 Uranyl Nitrate and its Complexes; their Role in Processing Nuclear Waste

Reaction of uranium oxide with nitric acid results in the formation of nitrates  $\text{UO}_2(\text{NO}_3)_{2 \cdot x} \text{H}_2\text{O}$  ( $x = 2, 3, 6$ ); the value of  $x$  depends upon the acid concentration. All contain  $[\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2]$  molecules; the nitrate groups are bidentate, so that uranium is 8 coordinate (Figure 11.5). Its most important property lies in its high solubility in a range of organic solvents in addition to water (Table 11.4), which is an important factor in the processing of nuclear waste.

**Table 11.4** Solubility of uranyl nitrate in various solvents

Solvent	Solubility (g per g solvent)
Water	0.540
Diethyl ether	0.491
Acetone	0.617
Ethanol	0.675

By adding metal nitrates as ‘salting out’ agents, the solubility of uranyl nitrate in water can be decreased to favour its extraction from aqueous solution into the organic layer. Tributyl phosphate [TBP;  $(\text{C}_4\text{H}_9\text{O})_3\text{P}=\text{O}$ ] acts as a complexing agent (in the manner discussed in this chapter for a number of phosphine oxide ligands) and also as solvent, with no salting-out agent being needed. In practice, a solution of TBP in kerosene is used to give better separation, as pure TBP is too viscous and also has a rather similar density to that of water.

### 11.5.5 Nuclear Waste Processing

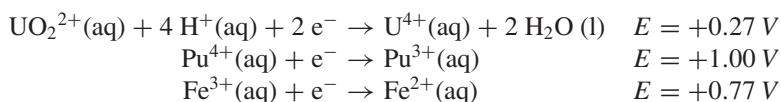
Nuclear fuel rods consist of uranium oxide pellets contained in zirconium alloy or steel tubes. As the fission process proceeds, uranium is used up and fission products accumulate. A lot of these fission products are good neutron absorbers and reduce the efficiency of the fission process (by absorbing neutrons before they reach uranium atoms) so that the rods are removed for reprocessing before all the  $^{235}\text{U}$  content has undergone fission. Fission of a  $^{235}\text{U}$  atom produces two lighter atoms of approximate relative atomic masses around 90–100 and 130–140, with the main fission products being the intensely radioactive and short lived  $^{131}\text{I}$  ( $t_{1/2} \sim 8$  d),  $^{140}\text{La}$ ,  $^{141}\text{Ce}$ ,  $^{144}\text{Pr}$ ,  $^{95}\text{Zr}$ ,  $^{103}\text{Ru}$ , and  $^{95}\text{Nb}$ , and longer-lived  $^{137}\text{Cs}$ ,  $^{90}\text{Sr}$ , and  $^{91}\text{Y}$ . These essentially useless and toxic products have to be separated from unchanged uranium and also from plutonium (the product of neutron absorption by  $^{238}\text{U}$ ), both of which can be used again as fuels.

1. The first stage of the process involves immersing the fuel rods in ponds of water for up to 3 months. This allows the majority of the short-lived and intensely radioactive fission products such as  $^{131}\text{I}$  to decay.

2. The rods are then dissolved in rather concentrated (7M) nitric acid, producing a mixture of  $\text{UO}_2(\text{NO}_3)_2$ ,  $\text{Pu}(\text{NO}_3)_4$ , and other metal nitrates.

3. The mixture is extracted with a counter-current of a solution of TBP in kerosene. Uranium and plutonium are extracted into kerosene as the complexes  $[\text{UO}_2(\text{NO}_3)_2(\text{tbp})_2]$  and  $[\text{Pu}(\text{NO}_3)_4(\text{tbp})_2]$ , but the other nitrates, of metals such as the lanthanides and actinides beyond Pu, as well as fission products, do not form strong complexes with TBP and stay in the aqueous layer.

4. The mixture of uranium and plutonium is treated with a suitable reducing agent [iron(II) sulfamate, hydrazine, or hydroxylamine nitrate]; under these conditions,  $\text{U}^{\text{VI}}$  is not reduced and stays in the kerosene layer, but  $\text{Pu}^{\text{IV}}$  is reduced to  $\text{Pu}^{3+}$ , which is only weakly complexed by TBP and so migrates into the aqueous phase.



The uranyl nitrate is extracted back into the aqueous phase and crystallized as the hydrate  $\text{UO}_2(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ ; thermal decomposition to  $\text{UO}_3$  is followed by hydrogen reduction to re-form  $\text{UO}_2$ . The plutonium is reoxidized to  $\text{Pu}^{4+}$ , precipitated as the oxalate  $\text{Pu}(\text{C}_2\text{O}_4)_2 \cdot 6\text{H}_2\text{O}$ , which undergoes thermal decomposition to  $\text{PuO}_2$ .

The fission products remain to be dealt with. The preferred solution at the moment is to evaporate their solution and pyrolyse the product to convert it into a mixture of oxides; on fusion with silica and borax an inert borosilicate glass is formed, which encapsulates the radioactive materials. At present the main problem seems to be choosing suitably stable geological areas where these materials will not be disturbed by earthquakes nor dissolved by underground water.

## 11.6 Complexes of the Actinide(IV) Nitrates and Halides

### 11.6.1 Thorium Nitrate Complexes

A number of thorium nitrate complexes have been synthesized and studied. Hydrated thorium nitrate,  $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ , contains  $[\text{Th}(\text{NO}_3)_4 \cdot (\text{H}_2\text{O})_3]$  molecules and was one of the first 11-coordinate compounds to be recognized (Figure 11.6).

Reaction of thorium nitrate with tertiary phosphine oxides in solvents like acetone or ethanol has afforded a number of complexes. In particular, when thorium nitrate reacts with  $\text{Me}_3\text{PO}$ , a wide range of complexes is obtained depending upon the stoichiometry and solvent used, compounds with formulae  $\text{Th}(\text{NO}_3)_4 \cdot 5\text{Me}_3\text{PO}$ ,  $\text{Th}(\text{NO}_3)_4 \cdot 4\text{Me}_3\text{PO}$ ,  $\text{Th}(\text{NO}_3)_4 \cdot 3.67\text{Me}_3\text{PO}$ ,  $\text{Th}(\text{NO}_3)_4 \cdot 3\text{Me}_3\text{PO}$ ,  $\text{Th}(\text{NO}_3)_4 \cdot 2.67\text{Me}_3\text{PO}$ , and  $\text{Th}(\text{NO}_3)_4 \cdot 2.33\text{Me}_3\text{PO}$  having been obtained. Thorium nitrate complexes display a fascinating range of structure (Table 11.5).

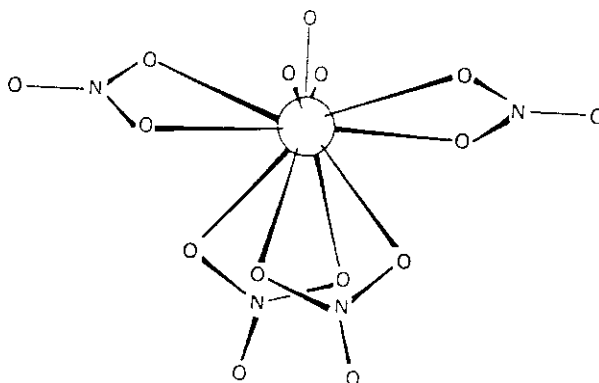
### 11.6.2 Uranium(IV) Nitrate Complexes

Uranium(VI) nitrate complexes have been discussed in Section 11.5.4, but uranium forms complexes in the +4 state that are generally similar to those of thorium.



**Table 11.5** Thorium nitrate complexes

Formula	Thorium species present	Coord. No.
MTh(NO <sub>3</sub> ) <sub>6</sub> (M = Mg, Ca)	[Th(NO <sub>3</sub> ) <sub>6</sub> ] <sup>2-</sup>	12
Ph <sub>4</sub> P <sup>+</sup> [Th(NO <sub>3</sub> ) <sub>5</sub> (OPMe <sub>3</sub> ) <sub>2</sub> ] <sup>-</sup>	[Th(NO <sub>3</sub> ) <sub>5</sub> (OPMe <sub>3</sub> ) <sub>2</sub> ] <sup>-</sup>	12
Th(NO <sub>3</sub> ) <sub>4</sub> ·5H <sub>2</sub> O	[Th(NO <sub>3</sub> ) <sub>4</sub> (H <sub>2</sub> O) <sub>3</sub> ]	11
Th(NO <sub>3</sub> ) <sub>4</sub> ·2.67Me <sub>3</sub> PO	{[Th(NO <sub>3</sub> ) <sub>3</sub> (Me <sub>3</sub> PO) <sub>4</sub> ] <sup>+</sup> } <sub>2</sub> [Th(NO <sub>3</sub> ) <sub>6</sub> ] <sup>2-</sup>	10, 12
Th(NO <sub>3</sub> ) <sub>4</sub> ·2Ph <sub>3</sub> PO	[Th(NO <sub>3</sub> ) <sub>4</sub> (OPPh <sub>3</sub> ) <sub>2</sub> ]	10
Th(NO <sub>3</sub> ) <sub>4</sub> ·5Me <sub>3</sub> PO	[Th(NO <sub>3</sub> ) <sub>2</sub> (OPMe <sub>3</sub> ) <sub>5</sub> ] <sup>2+</sup>	9

**Figure 11.6**  
Structure of Th(NO<sub>3</sub>)<sub>4</sub>(H<sub>2</sub>O)<sub>3</sub>.

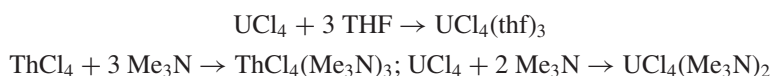
The reaction is carried out in a non-polar solvent like propanone; precipitated caesium nitrate is filtered off and green (the most characteristic colour of U<sup>IV</sup> complexes) crystals of the nitrate complex are obtained on concentrating the solution. U(NO<sub>3</sub>)<sub>4</sub>(OPPh<sub>3</sub>)<sub>2</sub> has a 10-coordinate structure (Figure 11.7) with phosphine oxide ligands *trans* to each other, and bidentate nitrates.

### 11.6.3 Complexes of the Actinide(IV) Halides

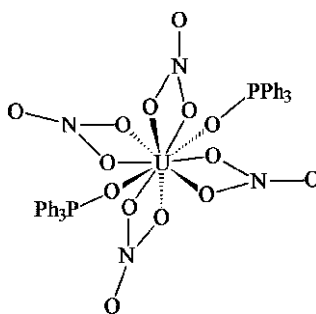
A large number of these have been synthesized, usually by reaction of the halides with the ligand in a non-polar solvent like MeCN or acetone, which will form a labile complex such as [UCl<sub>4</sub>(MeCN)<sub>4</sub>] that will undergo ready substitution by a stronger donor:



Although sometimes direct reaction with a liquid ligand is possible:



Relatively few UI<sub>4</sub> complexes have been made. They can often be synthesized by reaction in a solvent like MeCN and, whilst relatively stable thermally, undergo ready oxidation to uranyl complexes in (moist) air. The structures of many of these compounds have been determined, such as UCl<sub>4</sub>L<sub>2</sub> [L = Ph<sub>3</sub>PO, (Me<sub>2</sub>N)<sub>3</sub>PO, Et<sub>3</sub>AsO, (Me<sub>2</sub>N)<sub>2</sub>PhPO] and UBr<sub>4</sub>L<sub>2</sub> [L = Ph<sub>3</sub>PO, (Me<sub>2</sub>N)<sub>3</sub>PO] and UX<sub>4</sub>[(Me<sub>2</sub>N)<sub>2</sub>CO]<sub>2</sub> (X = Cl, Br, I). Both the 2:1 stoichiometry and *trans*-UX<sub>4</sub>L<sub>2</sub> geometry are very common, but there are

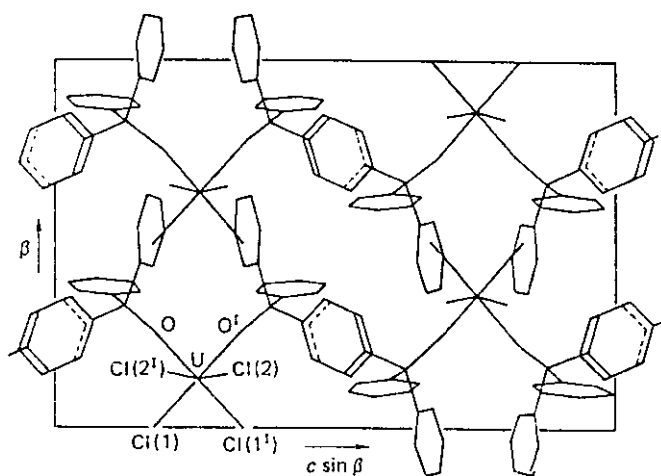


**Figure 11.7**  
Structure of  $\text{U}(\text{NO}_3)_4(\text{Ph}_3\text{PO})_2$ .

exceptions.  $\text{UCl}_4(\text{Me}_2\text{SO})_3$  is  $[\text{UCl}_2(\text{Me}_2\text{SO})_6]\text{UCl}_6$  and  $\text{UCl}_4(\text{Me}_3\text{PO})_6$  is  $[\text{UCl}(\text{Me}_3\text{PO})_6]\text{Cl}_3$ ; although no X-ray study has been carried out,  $\text{UI}_4(\text{Ph}_3\text{AsO})_2$  is almost certainly  $[\text{UI}_2(\text{Ph}_3\text{AsO})_4]\text{UI}_6$ .

Most structural reports concern uranium complexes. Many cases are known where complexes  $\text{MX}_4\text{L}_n$  ( $n$  usually 2) exist for some or all the series Th–Pu; they are generally believed to have the same structure.  $\text{UCl}_4(\text{Ph}_3\text{PO})_2$  is an exceptional compound in having a *cis* geometry, confirmed by X-ray diffraction studies on crystals obtained on recrystallization from nitromethane (Figure 11.8). The phenyl rings in neighbouring  $\text{Ph}_3\text{PO}$  molecules face each other with a ring–ring separation of  $\sim 3.52 \text{ \AA}$ , an early recognized example of  $\pi$ – $\pi$  stacking in a coordination compound. Similar compounds can be obtained for Th, Pa, Np, and Pu.

It was subsequently noted that crystals obtained immediately from the reaction mixture had an IR spectrum different to that of authentic *cis*- $\text{UCl}_4(\text{Ph}_3\text{PO})_2$  but strongly resembling those of samples of *trans*- $\text{UBr}_4(\text{Ph}_3\text{PO})_2$ . It seems likely that a less soluble *trans*- $\text{UCl}_4(\text{Ph}_3\text{PO})_2$  crystallizes first but on recrystallization or contact with the mother liquor it isomerizes to the thermodynamically more stable *cis*- $\text{UCl}_4(\text{Ph}_3\text{PO})_2$ .



**Figure 11.8**  
Reproduced with permission from JCS Dalton, (1975) 1875. G. Bombieri et al. Copyright (1975) RSC.

**Table 11.6** Bond lengths in  $UX_4L_2$  complexes

	$UCl_4(tmu)_2$	$UBr_4(tmu)_2$	$UI_4(tmu)_2$	$UCl_4(hmpa)_2$	$UBr_4(hmpa)_2$
Average U–O (Å)	2.209	2.197	2.185	2.23	2.18
Average U–X (Å)	2.62	2.78	3.01	2.615	2.781

Abbreviations:  $tmu = (Me_2N)_2C=O$ ;  $hmpa = (Me_2N)_3P=O$ .

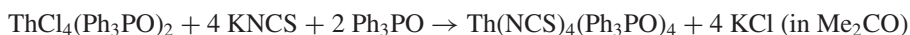
The only complete family of  $UX_4$  complexes ( $X = Cl, Br, I$ ) that has been examined crystallographically is that with tetramethylurea,  $UX_4[(Me_2N)_2CO]_2$ . Table 11.6 lists structural data for these compounds and also for  $UX_4[(Me_2N)_3PO]_2$  ( $X = Cl, Br$ ) {though the compound  $UI_4[(Me_2N)_3PO]_2$  has been made, its structure is not known}. Table 11.7 shows the formulae of  $ThCl_4$  and  $UCl_4$  complexes with the same ligands. The ionic radius of  $U^{4+} = 1.00$  Å and that of  $Th^{4+} = 1.05$  Å (values given for eight coordination, the pattern is similar for six coordination). Since the ions are of similar size, complexes usually have similar stoichiometry (and indeed geometry). In a few cases ( $Me_3N$ ,  $Ph_3PO$ , THF) the slightly greater size of thorium allows one more ligand to be attached to the metal ion.

**Table 11.7** A comparison of thorium(IV) and uranium(IV) complexes isolated with the same ligand

Ligand	Thorium	Uranium
MeCN	$ThCl_4(MeCN)_4$	$UCl_4(MeCN)_4$
$Ph_3PO$	$ThCl_4(Ph_3PO)_3$ ; $ThCl_4(Ph_3PO)_2$	$UCl_4(Ph_3PO)_2$
$(Me_2N)_3PO$	$ThCl_4[(Me_2N)_3PO]_3$ ; $ThCl_4[(Me_2N)_3PO]_2$	$UCl_4[(Me_2N)_3PO]_2$
$(Me_2N)_2CO$	$ThCl_4[(Me_2N)_2CO]_3$	$UCl_4[(Me_2N)_2CO]_2$
$Ph_2SO$	$ThCl_4(Ph_2SO)_4$	$UCl_4(Ph_2SO)_4$ ; $UCl_4(Ph_2SO)_3$
thf	$ThCl_4(thf)_3(H_2O)$	$UCl_4(thf)_3$
$Me_3N$	$ThCl_4(Me_3N)_3$	$UCl_4(Me_3N)_2$
$Me_2N(CH_2)_2NMe_2$	$ThCl_4[Me_2N(CH_2)_2NMe_2]_2$	$UCl_4[Me_2N(CH_2)_2NMe_2]_2$
$Me_2P(CH_2)_2PMe_2$	$ThCl_4[Me_2P(CH_2)_2PMe_2]_2$	$UCl_4[Me_2P(CH_2)_2PMe_2]_2$

## 11.7 Thiocyanates

As the anhydrous actinide thiocyanates are not known {only hydrated  $[M(NCS)_4(H_2O)_4]_x$ }, thiocyanate complexes are prepared metathetically.



The precipitate of insoluble KCl is filtered off and the solution concentrated to obtain the actinide complex. Several structures have been reported;  $Th(NCS)_4(L)_4$  [ $L = Ph_3PO$ ,  $(Me_2N)_3PO$ ];  $U(NCS)_4(L)_4$  [ $L = Ph_3PO$ ,  $(Me_2N)_3PO$ ,  $Me_3PO$ ] are all square antiprismatic;  $Th(NCS)_4[(Me_2N)_2CO]_4$  is dodecahedral.

Some complexes are known where thiocyanate is the only ligand bound to uranium. The geometry of  $(Et_4N)_4 [U(NCS)_8]$  is cubic, whilst  $Cs_4 [U(NCS)_8]$  is square antiprismatic. Compared with the d-block transition metals, there is not much evidence for directional character in bonding in lanthanide and actinide compounds. Because of this, the size and geometry of the cation affects the packing arrangements in the lattice and energetically this factor must be more important than any crystal-field effects favouring a particular shape of the anion.

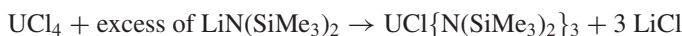
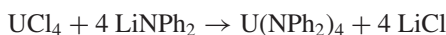
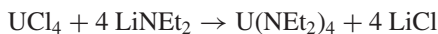


## 11.8 Amides, Alkoxides and Thiolates

Compounds  $\text{U}(\text{NR}_2)_x$  and  $\text{U}(\text{OR})_x$  have been synthesized in oxidation states +3 to +6 (though the hexavalent amides are not well characterized). A limited number of thiolates  $\text{U}(\text{SR})_4$  are also known. These largely molecular species occupy a borderline between classical coordination chemistry and organometallic chemistry.

### 11.8.1 Amide Chemistry

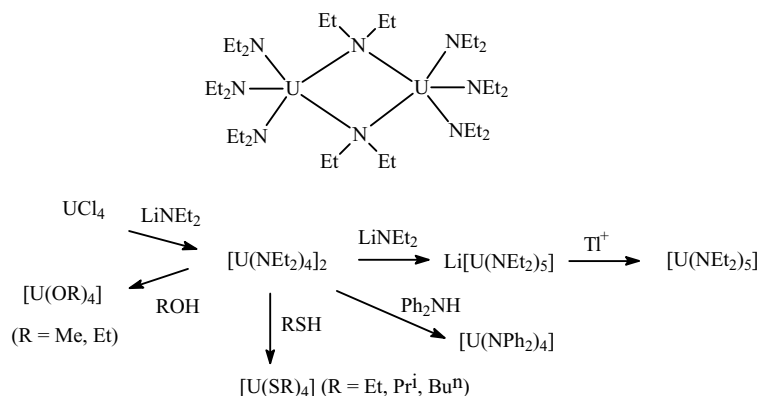
Although they have been much less studied than the range of alkoxides in the +4, +5, and +6 oxidation states, a number of amides of uranium(IV) have been made by ‘salt-elimination’ reactions in solvents such as diethyl ether or THF, examples being:



The steric demands of the ligands can be quantified in terms of the steric coordination number,  $\text{CN}_\text{S}$  [see J. Marçalo and A. Pires de Matos, *Polyhedron*, 1989, **8**, 2431;  $\text{CN}_\text{S}$  = the ratio of the solid angle comprising the Van der Waals’ spheres of the atoms of the ligand and that of the chloride ligand, when placed at a typical distance from the metal, values for these amide groups are:  $\text{NEt}_2^-$  1.67;  $\text{NPh}_2^-$  1.79;  $\text{N}(\text{SiMe}_3)_2^-$  2.17].

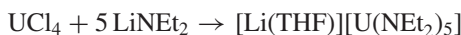
$\text{U}(\text{NPh}_2)_4$  is a monomer with a tetrahedral geometry, whilst in the solid state  $\text{U}(\text{NEt}_2)_4$  is actually a dimer,  $[\text{U}_2(\text{NEt}_2)_{10}]$ , which contains five-coordinate uranium, with two bridging amides (Figure 11.9). As  $\text{N}(\text{SiMe}_3)_2$  is a much bulkier ligand with larger solid cone angle, it seems likely that there is not room for a fourth amide group round uranium, hence the non-isolation of  $\text{U}\{\text{N}(\text{SiMe}_3)_2\}_4$ , with  $\text{MCl}\{\text{N}(\text{SiMe}_3)_2\}_3$  ( $\text{M} = \text{Th}, \text{U}$ ) being the most substituted species obtained; the halogen can be replaced by other groups such as methyl or tetrahydroborate. The compound  $\text{U}(\text{NMe}_2)_4$  is harder to prepare. In the solid state it has a chain trimeric structure; each uranium is 6 coordinate,  $\text{NMe}_2$  being less bulky than the other amides and has a smaller steric coordination number than even  $\text{NEt}_2$ .

So far, the amides described have all been in the +4 state, but one rare three coordinate  $\text{U}^{\text{III}}$  compound is  $\text{U}\{\text{N}(\text{SiMe}_3)_2\}_3$  (pyramidal, like the lanthanide analogues). Unusual amides



**Figure 11.9**  
Synthesis, structure and reaction of  $\text{U}(\text{NEt}_2)_4$ .

have also been prepared with uranium in the +5 and +6 oxidation states. The first step in the syntheses involved preparing anionic complexes with saturated coordination spheres:

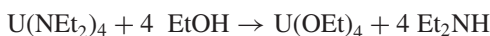


The anions can then be oxidized to neutral molecular species using TIBPh<sub>4</sub> or, better, AgI:



[U(NEt<sub>2</sub>)<sub>5</sub>] (which can be obtained as dark red crystals) is a monomer in benzene solution whilst [U(NMe<sub>2</sub>)<sub>6</sub>] is only known in solution. [U(NMe<sub>2</sub>)<sub>6</sub>] would be expected to be octahedral and [U(NEt<sub>2</sub>)<sub>5</sub>] trigonal bipyramidal, but no structures are known. The most versatile of all these compounds is U(NEt<sub>2</sub>)<sub>4</sub>. This is a low-melting (36 °C) and thermally stable substance (but like all alkoxides and alkylamides, immediately attacked by air or water). It can be distilled at ~40 °C at 10<sup>-4</sup> mmHg pressure and on account of this volatility was investigated for some time as a possible material for isotopic separation of uranium by gaseous diffusion. U(NEt<sub>2</sub>)<sub>4</sub> is a useful starting material for the synthesis of other amides, alkoxides, and thiolates (Figure 11.9)

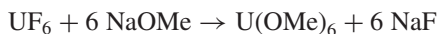
Its utility stems from the fact that alcohols and thiols are better proton donors (more acidic) than amines, thus:



### 11.8.2 Alkoxides and Aryloxides

U(OR)<sub>n</sub> compounds (R = alkyl or aryl) exist in oxidation states between +3 and +6; in addition, there are some uranyl alkoxides. An unusual feature is the number of thermally stable compounds in the otherwise unstable and rare +5 state.

A few uranyl alkoxides have been made, such as golden yellow [UO<sub>2</sub>(OCHPh<sub>2</sub>)<sub>2</sub>(thf)<sub>2</sub>], but more important are the large number of octahedral U(OR)<sub>6</sub> compounds that can be made, examples being U(OMe)<sub>6</sub>, U(OPr<sup>i</sup>)<sub>6</sub>, U(OBu<sup>t</sup>)<sub>6</sub>, U(OCF<sub>2</sub>CF<sub>3</sub>)<sub>6</sub>, and U(OCH<sub>2</sub>Bu<sup>t</sup>)<sub>6</sub> (U–O 2.001–2.002 Å).

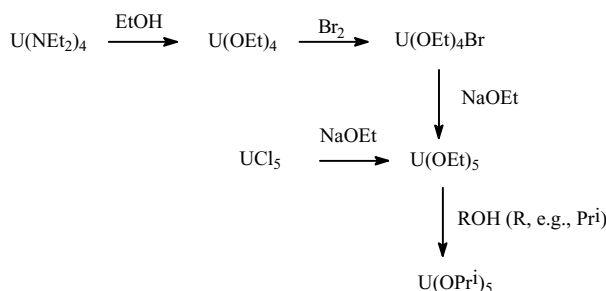


These compounds are volatile *in vacuo*, U(OCF<sub>2</sub>CF<sub>3</sub>)<sub>6</sub> remarkably boiling at 25 °C at 10 mmHg pressure. U(OMe)<sub>6</sub>, which sublimates at 30 °C at 10<sup>-5</sup> mmHg pressure, was investigated as a candidate for IR laser photochemistry leading to uranium isotopic enrichment.

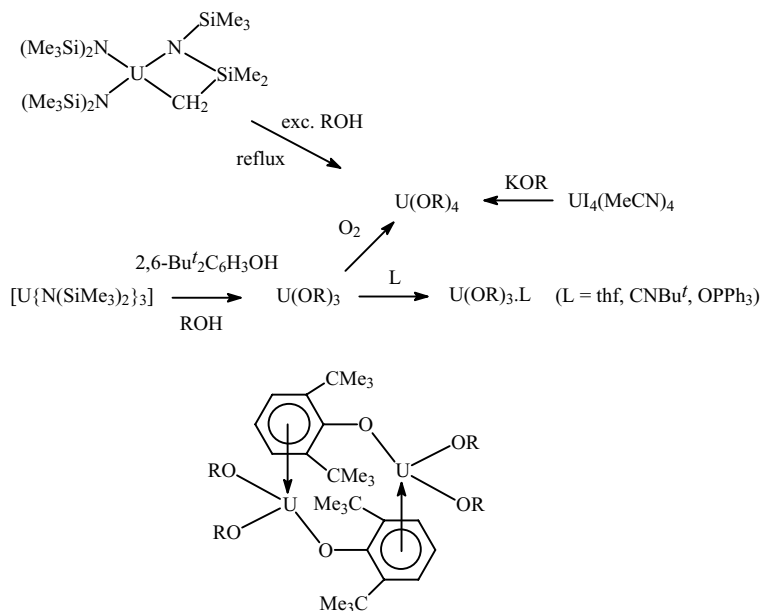
Unlike the monomeric U(OR)<sub>6</sub>, U(OR)<sub>5</sub> are usually associated; U(OPr<sup>i</sup>)<sub>5</sub> is dimeric with two alkoxide bridges giving six coordination. U(OEt)<sub>5</sub> is the easiest compound to synthesize and can be converted into others by alcohol exchange (Figure 11.10).

Uranium(IV) compounds tend to be non-volatile, highly associated solids, though the aryloxide U[O(2,6-Bu<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)]<sub>4</sub> is made of monomeric tetrahedral molecules, doubtless owing to its very bulky ligand. A number of U<sup>III</sup> aryloxide species have been synthesized, examples including U[O(2,6-Bu<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)]<sub>3</sub> being shown in Figure 11.11.

Since four of the same aryloxide ligands can bind to uranium in the uranium(IV) compound, a three coordinate U[O(2,6-Bu<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)]<sub>3</sub> is presumably coordinatively unsaturated, and so forms a uranium-ring bond; coordinative saturation can also be achieved by forming an adduct with a Lewis base.



**Figure 11.10**  
Synthesis of uranium alkoxides.



**Figure 11.11**  
Synthesis of uranium aryloxides.

## 11.9 Chemistry of Actinium

Little is known about the chemistry of actinium. It strongly resembles the lanthanides, especially lanthanum, with identical reduction potentials ( $\text{Ac}^{3+} + 3\text{e}^- \rightarrow \text{Ac}$ ;  $E = -2.62\text{ V}$ ) and similar ionic radii ( $\text{La}^{3+} = 106\text{ pm}$ ,  $\text{Ac}^{3+} = 111\text{ pm}$ ). Its chemistry is dominated by the (+3) oxidation state; as expected for a  $f^0$  ion, its compounds are colourless, with no absorption in the UV-visible region between 400 and 1000 nm.  $^{227}\text{Ac}$  is strongly radioactive ( $t_{1/2} = 21.77\text{ y}$ ) and so are its decay products. Most of the work carried out has been on the microgram scale, examining binary compounds such as the oxides and halides, and little is known about its complexes. Actinium metal itself is a silvery solid, obtained by reduction of the oxide, fluoride, or chloride with Group I metals; it is oxidized rapidly in moist air. Like lanthanum, it forms an insoluble fluoride (coprecipitating quantitatively with lanthanum on the tracer scale) and oxalate  $\text{Ac}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$ .

Since the chemistry of actinium is confined to the  $\text{Ac}^{3+}$  ion, it can readily be separated from thorium (and the lanthanides, for that matter) by processes like solvent extraction with thenoyltrifluoroacetone (TTFA) and by cation-exchange chromatography. The latter is an excellent means of purification, as the  $\text{Ac}^{3+}$  ion is much more strongly bound by the resin than its decay products.

## 11.10 Chemistry of Protactinium

Although its chemistry is not greatly studied at present, quite a lot of protactinium chemistry has been reported. The main isotope is the alpha-emitter  $^{231}\text{Pa}$ , which has a long half-life ( $t_{1/2} = 3.28 \times 10^4$  y) so few problems arise, once appropriate precautions are taken with the  $\alpha$ -emission, the only other point of note being the ready hydrolysis of  $\text{Pa}^{\text{V}}$  in solution. Protactinium metal itself, formed by reduction (Ba) of  $\text{PaF}_4$ , or thermal decomposition of  $\text{PaI}_5$  on a tungsten filament, is a high-melting ( $1565^\circ\text{C}$ ), dense ( $15.37\text{ g cm}^{-3}$ ), ductile silvery solid, which readily reacts on heating with many non-metals.

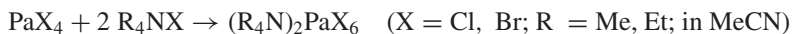
The aqueous chemistry is dominated by the readily hydrolysed  $\text{Pa}^{5+}$  ion, which in the absence of complexing ligands (e.g., fluoride) tends to precipitate as hydrated  $\text{Pa}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ . A  $\text{PaO}_2^+$  ion would be isoelectronic with the uranyl ion,  $\text{UO}_2^{2+}$ , but there is no evidence for it. However, solutions of  $\text{Pa}^{\text{V}}$  in fuming  $\text{HNO}_3$  yield crystals of  $\text{PaO}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$  ( $x = 1-4$ ), which may have  $\text{Pa}=\text{O}$  bonds; the sulfate  $\text{PaO}(\text{HSO}_4)_3$  also exists. Reduction of  $\text{Pa}^{\text{V}}$  with zinc or  $\text{Cr}^{2+}$  gives  $\text{Pa}^{4+}(\text{aq})$ , only stable in strongly acidic solution, as, at higher pH, ions like  $\text{Pa}(\text{OH})_2^{2+}$ ,  $\text{PaO}^{2+}$ , and  $\text{Pa}(\text{OH})_3^+$  are believed to exist.

Many of the complexes of Pa that have been studied are halide complexes, falling into two types; anionic species with all-halide coordination, and neutral Lewis base adducts, usually of the chloride  $\text{PaCl}_4$ .

Historically, the fluoride complexes are most important. Aristid Von Grosse (1934) used  $\text{K}_2\text{PaF}_7$  in his determination of the atomic mass of Pa in 1931. Colourless crystals of this and other complexes  $\text{MPaF}_6$ ,  $\text{M}_2\text{PaF}_7$ , and  $\text{M}_3\text{PaF}_8$  ( $\text{M} = \text{K}, \text{Rb}, \text{Cs}$ ) can be obtained by changing the stoichiometry, e.g.:



This complex has tricapped trigonal prismatic nine coordination of Pa, whilst  $\text{MPaF}_6$  has dodecahedral 8 coordination and  $\text{Na}_3\text{PaF}_8$  the very rare cubic 8 coordination. Other halide complexes can be made by appropriate methods:



Six-coordinate  $[\text{PaX}_6]^{2-}$  ions have been confirmed by X-ray diffraction for  $(\text{Me}_4\text{N})_2\text{PaX}_6$  ( $\text{X} = \text{Cl}, \text{Br}$ ) and  $\text{Cs}_2\text{PaCl}_6$ .

Many adducts of the tetrahalides of ligands like phosphine oxides have been synthesized by direct interaction of the tetrahalides with the ligands in solution in solvents like acetonitrile or propanone. These have similar stoichiometries and structures to analogous complexes of Th, U, Np, and Pu, examples being *trans*- $\text{PaX}_4[(\text{Me}_2\text{N})_3\text{PO}]_2$  ( $\text{X} = \text{Cl}, \text{Br}$ ); *cis*- $\text{PaCl}_4(\text{Ph}_3\text{PO})_2$ ;  $\text{PaCl}_4(\text{MeCN})_4$ ;  $\text{PaCl}_4(\text{Me}_2\text{SO})_5$  {possibly  $[\text{PaCl}_3(\text{Me}_2\text{SO})_5]^+ \text{Cl}^-$ }

and  $\text{PaCl}_4(\text{Me}_2\text{SO})_3$  {possibly  $[\text{PaCl}_2(\text{Me}_2\text{SO})_6]^{2+} [\text{PaCl}_6]^{2-}$ }. In addition, a few adducts of the pentahalides,  $\text{PaX}_5(\text{Ph}_3\text{PO})_n$  ( $n = 1, 2$ ) exist.

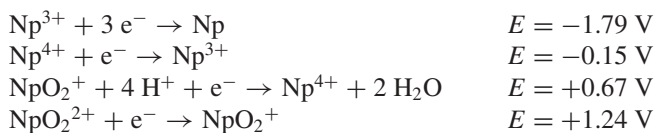
In addition to these, a number of other complexes have been isolated, such as the  $\beta$ -diketonates  $[\text{Pa}(\text{PhCOCHCOPh})_4]$  and antiprismatic  $[\text{Pa}(\text{MeCOCHCOMe})_4]$ , which, like the TTFA complex  $[\text{Pa}(\text{C}_4\text{H}_3\text{SCOCHCOF}_3)_4]$ , are soluble in solvents like benzene, and suitable for purification by solvent extraction. Pa forms a volatile borohydride  $[\text{Pa}(\text{BH}_4)_4]$ . These compounds are typical of those formed by other early actinides, such as Th and U.

## 11.11 Chemistry of Neptunium

The metal itself is a dense ( $19.5 \text{ g cm}^{-3}$ ) silvery solid, which readily undergoes oxidation in air. Chemical study uses one isotope, the long-lived  $^{237}\text{Np}$  ( $t_{1/2} = 2.14 \times 10^6 \text{ y}$ ). The chemistry of neptunium shows interesting points of comparison between U and Pu, which flank it (and like them it shows a wide range of oxidation states). Thus, whilst the (+6) oxidation state is found in the  $[\text{NpO}_2]^{2+}$  ion as well as in the halide  $\text{NpF}_6$  (note that there is no  $\text{NpCl}_6$ , unlike U), the (+6) state is less stable than in the case of uranium, though it is more stable than  $\text{Pu}^{\text{VI}}$ . However, the (+5) state is more stable for neptunium than for uranium, with the  $[\text{NpO}_2]^+$  ion showing no signs of disproportionation, though easily undergoing reduction by  $\text{Fe}^{2+}$  to  $\text{Np}^{4+}$ .

$\text{Np}^{4+}$  is in many ways the most important oxidation state. It is formed by reduction of the higher oxidation states, and by aerial oxidation of  $\text{Np}^{3+}$ . Strong oxidizing agents like  $\text{Ce}^{4+}$  oxidize it back to  $[\text{NpO}_2]^{2+}$ , whilst electrolytic reduction of  $\text{Np}^{4+}$  affords  $\text{Np}^{3+}$ , which is stable in the absence of air (unlike U).

As neptunium has one more outer-shell electron than uranium, it has the possibility of a (+7) oxidation state, a possibility realized in alkaline solution, when ozone will oxidize  $\text{Np}^{\text{VI}}$  to  $\text{Np}^{\text{VII}}$ , an oxidation also achieved by  $\text{XeO}_3$  or  $\text{IO}_4^-$  at higher temperatures. The potential for this is estimated as  $-1.24 \text{ V}$  (1M alkali). The relevant standard potentials for neptunium (1M acid) are:



### 11.11.1 Complexes of Neptunium

A significant amount of structural information has been gathered on neptunium complexes. For the main, they resemble corresponding U and Pu complexes. However, an EXAFS study of alkaline solutions of  $\text{Np}^{\text{VII}}$  found evidence for a *trans* dioxo ion of the type  $[\text{NpO}_2(\text{OH})_4(\text{OH}_2)]^{1-}$ .

In the VI state, the 8 coordinate  $\text{Na}[\text{NpO}_2(\text{OAc})_3]$ ,  $[\text{NpO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$ ,  $\text{K}_4[\text{NpO}_2(\text{CO}_3)_3]$ , and  $\text{Na}_4[\text{NpO}_2(\text{O}_2)_3] \cdot 9\text{H}_2\text{O}$  [where  $(\text{O}_2)_3$  indicates three peroxide dianion ligands] are isostructural with the U, Pu, and Am analogues. They demonstrate a contraction of  $\sim 0.01 \text{ \AA}$  in the  $\text{M}=\text{O}$  distance per unit increase in atomic number. Eight coordination is also found in  $[\text{NpO}_2(\text{NO}_3)_2(\text{bipy})]$ . The aqua ion appears to be seven

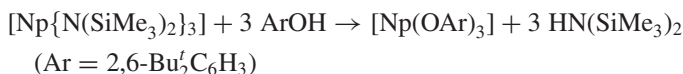
coordinate  $[\text{NpO}_2(\text{H}_2\text{O})_5]^{2+}$ . Like the uranyl ion, the neptunyl ion complexes with expanded porphyrins like hexaphyrin, amethyrin, pentaphyrin, and alaskaphyrin.

In the  $\text{Np}^{\text{V}}$  state, structural comparison of  $\text{Ba}[\text{Np}^{\text{V}}\text{O}_2(\text{OAc})_3]$  with  $\text{Na}[\text{Np}^{\text{VI}}\text{O}_2(\text{OAc})_3]$  indicates a lengthening of 0.14 Å in the neptunium–oxygen bond length on going from  $\text{Np}^{\text{VI}}$  to  $\text{Np}^{\text{V}}$ , consistent with an electron added to an antibonding orbital. As with the V state, the aqua ion is believed to be seven coordinate  $[\text{NpO}_2(\text{H}_2\text{O})_5]^+$ ; in the related  $[\text{NpO}_2(\text{urea})_5](\text{NO}_3)$  the neptunium atom has a typical pentagonal-bipyramidal environment with five oxygen atoms in the equatorial plane. A similar geometry is found in the acetamide complex of neptunium v nitrate,  $[(\text{NpO}_2)(\text{NO}_3)(\text{CH}_3\text{CONH}_2)_2]$ , where the pentagonal bipyramidal coordination of Np is completed (in the solid state) using oxygens of neighbouring  $\text{NpO}_2$  groups; similarly in  $\text{NpO}_2\text{ClO}_4 \cdot 4\text{H}_2\text{O}$ , the neptunyl(v) ion has four waters and a distant neptunyl oxygen occupying the equatorial positions. Eight and six coordination are, respectively, found in the crown ether complex,  $[\text{NpO}_2(18\text{-crown-6})]\text{ClO}_4$ , and in  $[\text{NpO}_2(\text{OPPh}_3)_4]\text{ClO}_4$ . Carbonate complexes have been investigated as they could represent a means of leaching transactinides from underground deposits. EXAFS studies of  $\text{Np}^{\text{V}}$  carbonate complexes indicate the existence of  $[\text{NpO}_2(\text{H}_2\text{O})_3(\text{CO}_3)]^-$ ,  $[\text{NpO}_2(\text{H}_2\text{O})_2(\text{CO}_3)_2]^{3-}$  and  $[\text{NpO}_2(\text{CO}_3)_3]^{5-}$ ; similar  $\text{Np}^{\text{VI}}$  species like  $[\text{NpO}_2(\text{CO}_3)_3]^{4-}$  are indicated.

Among neptunium(vi) complexes,  $[\text{Np}(\text{S}_2\text{CNET}_2)_4]$  and  $[\text{Np}(\text{acac})_4]$  have dodecahedral and antiprismatic coordination of neptunium. A reminder of the small differences in energy between different geometries is that  $[\text{Me}_4\text{N}]_4$   $[\text{Np}(\text{NCS})_8]$  has tetragonal antiprismatic coordination, whilst  $[\text{Et}_4\text{N}]_4$   $[\text{Np}(\text{NCS})_8]$  has cubic coordination of Np. Neptunium(IV) is also eight coordinate in  $[\text{Np}(\text{urea})_8]\text{SiW}_{12}\text{O}_{40} \cdot 2\text{Urea} \cdot \text{H}_2\text{O}$ .

As with Th, Pa, U, and Pu, a variety of neutral complexes are formed between the tetrahalides (and nitrate) and ligands like phosphine oxides, such as *trans*- $[\text{NpX}_4\{(\text{Me}_2\text{N})_3\text{PO}\}_2]$  ( $\text{X} = \text{Cl}, \text{Br}$ ); *cis*- $[\text{NpCl}_4(\text{Ph}_3\text{PO})_2]$ ;  $\text{NpCl}_4(\text{Me}_2\text{SO})_3$  (possibly  $[\text{NpCl}_2(\text{Me}_2\text{SO})_6]^{2+}[\text{NpCl}_6]^{2-}$ );  $[\text{Np}(\text{NCS})_4(\text{R}_3\text{PO})_2]$  ( $\text{R} = \text{Ph}, \text{Me}, \text{Me}_2\text{N}$ ), and  $[\text{Np}(\text{NO}_3)_4(\text{Me}_2\text{SO})_3]$ .

Only a few complexes of  $\text{Np}^{\text{III}}$  have been characterized, notably the dithiocarbamate  $\text{Et}_4\text{N}[\text{Np}(\text{S}_2\text{CNET}_2)_4]$ , which has distorted dodecahedral coordination like the Pu and lanthanide analogues.  $[\text{NpI}_3(\text{thf})_4]$  and the silylamide  $[\text{Np}\{\text{N}(\text{SiMe}_3)_2\}_3]$  are analogous to those of U and the lanthanides, the former potentially being a useful starting material. The amide reacts with a bulky phenol:



## 11.12 Chemistry of Plutonium

Plutonium presents particular problems in its study. One reason is that, since  $^{239}\text{Pu}$  is a strong  $\alpha$ -emitter ( $t_{1/2} = 24,100$  years) and also tends to accumulate in bone and liver, it is a severe radiological poison and must be handled with extreme care. A further problem is that the accidental formation of a critical mass must be avoided.

### 11.12.1 Aqueous Chemistry

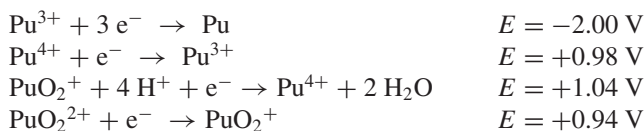
Because of the complicated redox chemistry, not all the oxidation states +3 to +7 are observed under all pH conditions. Blue  $\text{Pu}^{3+}(\text{aq})$  resembles the corresponding  $\text{Ln}^{3+}$  ions whilst the brown  $\text{Pu}^{4+}$  ion requires strongly acidic conditions (6M) to prevent oligomerization

and disproportionation. The purple-pink  $\text{PuO}_2^+$  ion readily disproportionates, whilst the orange-yellow  $\text{PuO}_2^{2+}$  ion resembles the uranyl ion, but is less stable, tending to be reduced, not least by its own  $\alpha$ -decay. Blue  $\text{Pu}^{\text{VII}}$ , possibly  $\text{PuO}_5^{3-}(\text{aq})$  or some oxo/hydroxy species like  $[\text{PuO}_2(\text{OH})_4(\text{OH}_2)]^{3-}$ , exists only at very high pH; it is formed by ozonolysis of  $\text{Pu}^{\text{VI}}$ , and some  $\text{Pu}^{\text{VIII}}$  may be generated.

### 11.12.2 The Stability of the Oxidation States of Plutonium

In comparison with uranium, the (+3) state has become much more stable (Table 9.5), witness the standard reduction potential of +0.98 V for  $\text{Pu}^{4+} + \text{e}^- \rightarrow \text{Pu}^{3+}$ , the comparative value for uranium being  $-0.63$  V. This means that quite strong oxidizing agents such as manganate(VII) are needed to effect this oxidation in the case of plutonium.

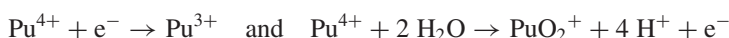
The relevant standard potentials for plutonium are:



The  $\text{Pu}^{\text{III}}\text{--Pu}^{\text{IV}}$  and the  $\text{Pu}^{\text{V}}\text{--Pu}^{\text{VI}}$  couples are both reversible, but not the  $\text{Pu}^{\text{IV}}\text{--Pu}^{\text{V}}$ , as the latter involves the making and breaking of  $\text{Pu}=\text{O}$  bonds and significant changes in geometry (cf. uranium). Reactions involving the making and breaking of  $\text{Pu}=\text{O}$  bonds are also kinetically slow, so that it is possible for ions in all four oxidation states between (+3) and (+6) to coexist in aqueous solution under certain conditions. The even spacing of the potentials linking the four oxidation states means that disproportionation and reproporationation reactions are feasible. For example, a possible route for disproportion of  $\text{Pu}^{4+}$  in aqueous solution can be written:



This is composed of two redox processes:



Because the potentials are of roughly equal magnitude (and of opposite sign in this case), the free energy change is small ( $<20 \text{ kJmol}^{-1}$ ). The following process:



is also favoured; overall, the two can be combined as:

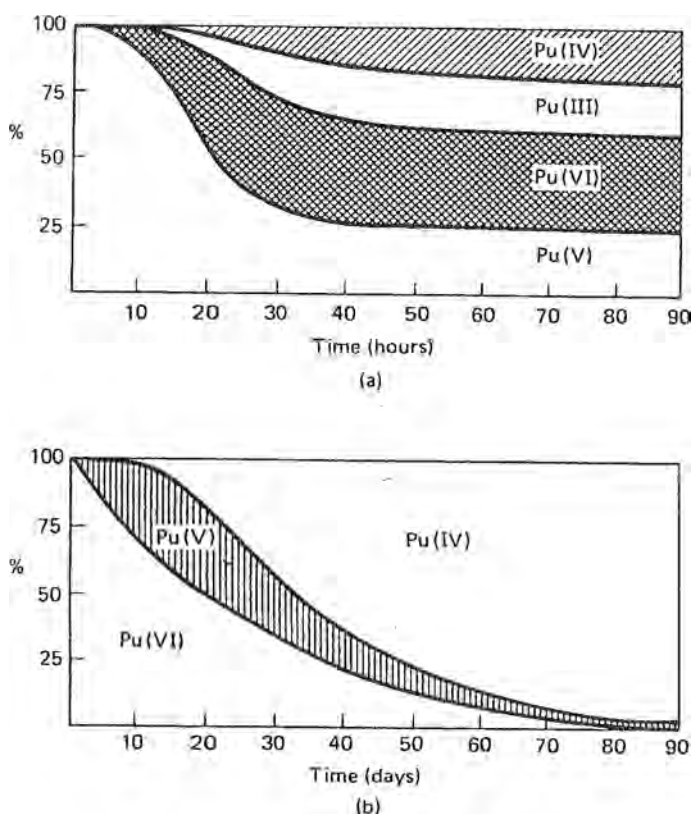


Another feasible reproporationation reaction is of course:



A further problem is that compounds in the +5 and +6 oxidation states tend to be reduced (autoradiolysis), as  $^{239}\text{Pu}$  is a strong  $\alpha$ -emitter (1 mg  $^{239}\text{Pu}$  emits over a million  $\alpha$ -particles a second) decomposing water molecules into  $\bullet\text{H}$ ,  $\bullet\text{OH}$  and  $\bullet\text{O}$  radicals which, in turn, participate in redox reactions. In acidic solution, decomposition of the solvent to  $\text{H}_2\text{O}_2$  and the acid can occur. In nitric acid, for example, both  $\text{HNO}_2$  and nitrogen oxides are formed, so that, starting with plutonium(VI), ions in the lower oxidation states are generated





**Figure 11.12**

(a) Disproportionation of  $\text{Pu}^{\text{V}}$  in 0.1M  $\text{HNO}_3$  + 0.2 M  $\text{NaNO}_3$ . (b) Self-reduction of  $\text{Pu}^{\text{VI}}$  due to its own  $\alpha$ -emission, in 5M  $\text{NaNO}_3$  (after P.I. Artiukhin, V.I. Medicedovskii, and A.D. Gel'man, *Radiokhimiya*, 1959, **1** 131; *Zh. Neorg. Khim.*, 1959, **4**, 1324) (permission applied for reproduction).

by both the reduction and disproportionation/reproportionation reactions described above. Figure 11.12 shows the effects of these processes. In Figure 11.12(a), the disproportionation of  $\text{Pu}^{\text{V}}$  into all the (+3) to (+6) states can be seen, whilst in Figure 11.12(b), over a longer time scale, the self-reduction of  $\text{Pu}^{\text{VI}}$  to  $\text{Pu}^{\text{IV}}$  is observed.

In perchloric acid, the (+4) state is less abundant, and the (+3) state more abundant, a reflection of the higher oxidizing power of nitric acid.

### 11.12.3 Coordination Chemistry of Plutonium

In its coordination chemistry, plutonium(VI) resembles uranium, where corresponding complexes exist. Thus crystallization of solutions of  $\text{Pu}^{\text{VI}}$  in concentrated nitric acid affords red-brown to purple crystals of the hexahydrate  $\text{PuO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , which is isostructural with the U analogue, and contains 8-coordinate  $[\text{PuO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2]$  molecules. An X-ray absorption spectroscopy study of tributyl phosphate complexes of  $[\text{AnO}_2(\text{NO}_3)_2]$  ( $\text{An} = \text{U}, \text{Np}, \text{Pu}$ ) in solution, probably present as  $[\text{AnO}_2(\text{NO}_3)_2(\text{tbp})_2]$ , has indicated major changes in the actinide's coordination sphere on reduction to the  $\text{An}^{\text{IV}}$  state, but no significant changes across the series  $\text{UO}_2^{2+}$ ,  $\text{NpO}_2^{2+}$ ,  $\text{PuO}_2^{2+}$ . An actinide contraction of

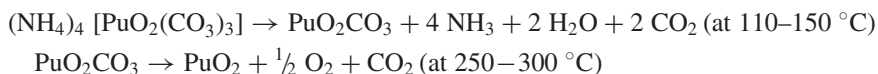


about 0.02 Å between successive actinides was detected ( $M = O$  changes overall from 1.79 to 1.75 Å on passing from U to Pu).

Adding acetate ions to a  $Pu^{VI}$  solution, in the presence of the appropriate Group I metal (M), results in precipitation of  $M [PuO_2(OAc)_3]$ , also 8 coordinate, with bidentate acetates, isostructural with the U, Np, and Am analogues. Other examples of polyhedra resembling the corresponding uranyl complexes are to be found in the  $[PuO_2Cl_4]^{2-}$  (*trans*-octahedral) and  $[PuO_2F_5]^{3-}$  (pentagonal bipyramidal) ions. Plutonium(VI) carbonate complexes are important in the preparation of ceramic materials. The  $PuO_2^{2+}$  ion is precipitated from aqueous solution by carbonate ion, but this is soluble in excess of carbonate.

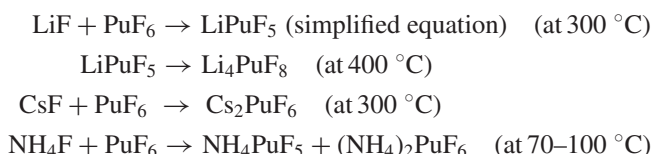


In the latter ion, Pu has (2 + 6) coordination {X-ray diffraction of  $[C(NH_2)_4][PuO_2(CO_3)_3]$ }. The ammonium salt undergoes two-stage thermal decomposition, via (the isolable)  $PuO_2CO_3$ :



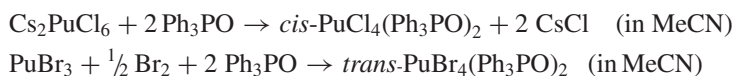
Few Pu(+5) compounds have been characterized in the solid state.

In the (+4) oxidation state, plutonium forms many halide complexes, both anionic and neutral, contrasting with the absence of  $PuCl_4$  and  $PuBr_4$  (though no iodides are known).  $Pu^{4+}(aq)$  reacts with conc. HX forming  $[PuX_6]^{2-}$  ions ( $X = Cl, Br$ ) isolable as salts such as  $(Et_4N)_2PuBr_6$  and  $Cs_2PuCl_6$ , both probably containing octahedrally coordinated Pu, and useful as starting materials for making  $Pu^{IV}$  halide complexes. Various fluoride complexes can be made, often relying on the instability of  $PuF_6$ :

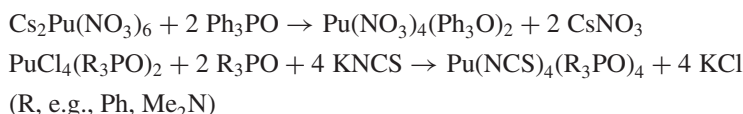


High coordination numbers are usual in fluoride complexes;  $(NH_4)_4PuF_8$  has nine-coordinate Pu.

Neutral halide complexes are usually got starting from  $[PuX_6]^{2-}$  salts ( $X = Cl, Br$ ), though bromides can also be made by bromine oxidation of  $Pu^{III}$  species.



A wide range of these complexes, also involving nitrate and thiocyanate ligands, has been made:



Others include *trans*- $PuX_4[(Me_2N)_3PO]_2$  ( $X = Cl, Br$ );  $PuCl_4(Ph_2SO)_n$  ( $n = 3, 4$ );  $PuCl_4(Me_2SO)_n$  ( $n = 3, 7$ );  $PuCl_4(Me_3PO)_6$  {probably  $[PuCl(Me_3PO)_6]^{3+} (Cl^-)_3$ }. Structurally, they resemble the corresponding complexes of Th, Pa, U, and Np. The tridentate

ligand 2,6-[Ph<sub>2</sub>P(O)CH<sub>2</sub>]<sub>2</sub>C<sub>5</sub>H<sub>3</sub>NO combines two phosphine oxide and one N-oxide functional groups; it forms a 2:1 Pu<sup>IV</sup> complex which has the same structure, [PuL<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub>, in both the solid state and solution. The 2:1 complex of the bidentate ligand 2-[Ph<sub>2</sub>P(O)CH<sub>2</sub>]<sub>2</sub>C<sub>5</sub>H<sub>4</sub>NO with plutonium nitrate also has an ionic structure [PuL<sub>2</sub>(NO<sub>3</sub>)<sub>3</sub>]<sub>2</sub>[Pu(NO<sub>3</sub>)<sub>6</sub>]. As is the case with uranium, nitrate complexes are important in the separation chemistry of plutonium. Solutions of Pu<sup>4+</sup>(aq) in conc. HNO<sub>3</sub> deposit dark green crystals of Pu(NO<sub>3</sub>)<sub>4</sub>·5H<sub>2</sub>O, which contain 11-coordinate [Pu(NO<sub>3</sub>)<sub>4</sub>(H<sub>2</sub>O)<sub>3</sub>] molecules (as is the case with Th). [Pu(NO<sub>3</sub>)<sub>6</sub>]<sup>2-</sup> ions can be fished out of very concentrated (10–14M) nitric acid solutions as salts R<sub>2</sub>Pu(NO<sub>3</sub>)<sub>6</sub> (R = Cs, Et<sub>4</sub>N). [Pu(NO<sub>3</sub>)<sub>6</sub>]<sup>2-</sup> is strongly adsorbed by anion-exchange resins, and this is made use of in the purification of Pu commercially.

Plutonium carbonate complexes are important as they contribute to an understanding of what happens to plutonium in the environment, Pu(+4) being the most stable oxidation state under normal conditions. [Pu(CO<sub>3</sub>)<sub>5</sub>]<sup>6-</sup> has been identified by EXAFS as the Pu<sup>IV</sup> species in solution at high carbonate concentration; the structure of crystalline [Na<sub>6</sub>Pu(CO<sub>3</sub>)<sub>5</sub>]<sub>2</sub>·Na<sub>2</sub>CO<sub>3</sub>·33H<sub>2</sub>O has also been determined; it features 10-coordinate plutonium. The sulfate complex K<sub>4</sub>Pu(SO<sub>4</sub>)<sub>4</sub>·2H<sub>2</sub>O contains dimeric [(SO<sub>4</sub>)<sub>3</sub>Pu(μ-SO<sub>4</sub>)<sub>2</sub>Pu(SO<sub>4</sub>)<sub>3</sub>]<sup>8-</sup> anions with nine-coordinate Pu.

In many aspects of its coordination chemistry, Pu<sup>IV</sup> compounds resemble their uranium analogues; thus it forms eight-coordinate complexes with diketonate ligands, like [Pu(acac)<sub>4</sub>], and similar complexes with 8-hydroxyquinolate and tropolonate. There is a limited alkoxide chemistry, [Pu(OBu<sup>t</sup>)<sub>4</sub>] being volatile at 112 °C (0.05 mmHg pressure) and very likely being a monomer. The borohydride [Pu(BH<sub>4</sub>)<sub>4</sub>] is a blue-black volatile liquid (mp 15 °C) and has a 12 coordinate molecular structure, with tridentate borohydride ligands, like the neptunium analogue, but unlike 14 coordinate [U(BH<sub>4</sub>)<sub>4</sub>].

Little coordination chemistry is as yet known in the (+3) state, but these compounds are interesting. Reaction of Pu with iodine in THF affords off-white [PuI<sub>3</sub>(thf)<sub>4</sub>], a useful starting material; [PuI<sub>3</sub>(dmsO)<sub>4</sub>] and [PuI<sub>3</sub>(py)<sub>4</sub>] have also been reported. The σ-alkyl [Pu{CH(SiMe<sub>3</sub>)<sub>2</sub>}]<sub>3</sub> and the silylamide [Pu{N(SiMe<sub>3</sub>)<sub>2</sub>}]<sub>3</sub> are analogous to those of U and the lanthanides, the latter potentially being a useful starting material (though neither has been completely characterized). The amide reacts with a bulky phenol forming the aryloxide [Pu(OAr)<sub>3</sub>] (Ar = 2,6-Bu<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), which is probably three coordinate. Plutonium forms insoluble oxalates Pu<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>·x H<sub>2</sub>O (x = 10, 11) similar to those of the lanthanides.

Reaction of plutonium metal with triflic acid affords blue Pu(CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, isostructural with the lanthanide triflates and which contains tricapped trigonal prismatic [Pu(H<sub>2</sub>O)<sub>9</sub>]<sup>3+</sup> ions; similarly, Pu reacts with AgPF<sub>6</sub> (or TlPF<sub>6</sub>) in MeCN suspension, dissolving to form [Pu(MeCN)<sub>9</sub>](PF<sub>6</sub>)<sub>3</sub>, in which the coordination polyhedron is rather more distorted.

#### 11.12.4 Plutonium in the Environment

Actinides are potentially present in the environment from a number of sources, not just the ‘natural’ thorium and uranium. Nuclear power plants and uses in nuclear weapons are obvious areas for concern, raised in recent times by possibilities that terrorist groups could gain control of such weapons, possibly ‘dirty’ bombs. Plutonium is an obvious source of concern. Any plutonium in the environment is believed to be largely present as rather insoluble Pu<sup>IV</sup> species. Pu<sup>IV</sup> ions are hydrolysed easily, unless in very acidic solution, forming light green colloidal species, which age with time, their solubility decreasing. The possibility of colloid-facilitated transport of plutonium occurring was raised by the observation of

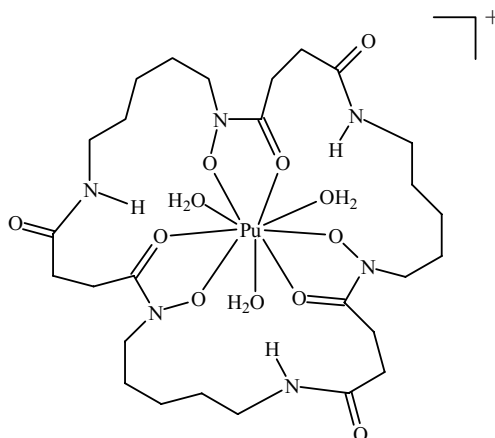
migration of plutonium in ground water by rather more than a mile from the location of underground weapons testing in Nevada, USA, over a period greater than 20 years. It is therefore necessary to consider the interaction of plutonium, not just with inorganic ions like carbonate (see Section 11.12.3), phosphate, silicate and sulfate, but with natural organic substances like humic acid.

Disposal of nuclear waste materials – especially the high-level waste from the cores of reactors and nuclear weapons – so that they do not escape into the environment is a pressing problem. Currently the preferred solution in the USA and most of Europe is immobilization in a suitable geological repository. The waste materials are evaporated if necessary, then heated with silica and borax to form a borosilicate glass, encased in an inert (e.g., lead) material, then buried in a stable zone, such as rock salt or clay. The conditions surrounding such sites are important. Yucca Mountain, Nevada, is the leading candidate among possible American sites. Solubility studies have shown that Np is more than 1000 times more soluble in the Yucca Mountain waters than is Pu, because under the ambient conditions Pu tends to adopt the (+4) state, associated with insolubility, whilst Np adopts the (+5) state, where compounds are much more soluble. However, at the WIPP site in New Mexico, which is built on a deep salt formation, the very salty brines favour formation of soluble Pu(+6) complexes such as  $[\text{PuO}_2\text{Cl}_4]^{2-}$ , which will present much more of a problem unless reducing conditions can be generated.

As a potential environmental hazard, plutonium is particularly toxic because of the remarkable similarity of  $\text{Pu}^{\text{IV}}$  and  $\text{Fe}^{\text{III}}$  – which means that Pu can be taken up in the biological iron transport and storage system of mammals. This similarity is being used in a biomimetic approach to Pu-specific ligands for both *in-vivo* actinide decorporation and nuclear waste remediation agents. It has also been suggested that plutonium could be solubilized by microbial siderophores. These are ligands used by bacteria to bind  $\text{Fe}^{3+}$  (an ion which, like  $\text{Pu}^{4+}$ , is essentially ‘insoluble’ at near-neutral pH) and carry it into cells. In fact, such siderophores bind plutonium strongly ( $\log \beta = 30.8$  for the desferrioxamine B complex), only taking it up as  $\text{Pu}^{\text{IV}}$  with plutonium in other oxidation states being oxidized or reduced appropriately. They do not solubilize plutonium rapidly, however; they are, in fact, less effective in solubilizing plutonium than are simple complexing agents like EDTA and citrate, leading to the suggestion that the siderophores passivate the surface of the plutonium hydroxide. (The overall formation constant for  $[\text{Pu-EDTA}]$  in acidic solution is  $\log \beta = 26.44$ ; the strength of the complexation means that the possibility of EDTA, widely used in former nuclear weapons programmes, solubilizing and transporting plutonium is a present concern).

Unlike the exclusively 6-coordinate iron(III) siderophore complexes, higher coordination numbers are possible with plutonium; the complex of  $\text{Pu}^{\text{IV}}$  with desferrioxamine E (DFE; a hexadentate iron-binding siderophore ligand) has shown it to contain 9-coordinate  $[\text{Pu}(\text{dfe})(\text{H}_2\text{O})_3]^+$  ions with a tricapped trigonal prismatic geometry (Figure 11.13).

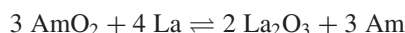
The microbe *Mycena flavescentis* has been found to take up Pu (but not U) in the form of a siderophore complex though at a much slower rate than it takes up iron; the Fe and Pu complexes inhibit each other, indicating competition for the same binding site on the microbe. It has similarly been found that pyoverdine, the main siderophore in iron-gathering capacity produced by *Pseudomonas aeruginosa*, will also transport plutonium across cell membranes. It has been suggested that using phytosiderophores such as desferrioxamine and mugineic acids could solubilize actinides and promote their uptake by plants and consequent removal from the soil.



**Figure 11.13**  
Structure of a  $\text{Pu}^{\text{IV}}$  complex of a siderophore.

## 11.13 Chemistry of Americium and Subsequent Actinides

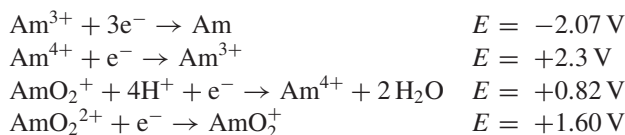
Two isotopes,  $^{241}\text{Am}$  ( $t_{1/2} = 433$  y), a decay product of  $^{241}\text{Pu}$ , and  $^{243}\text{Am}$  ( $t_{1/2} = 7380$  y), have half-lives suitable for their use in chemical reactions. The metal itself is a silvery, ductile and malleable solid, which is obtained by metallothermic (Ba, Li) reduction of the trifluoride; alternatively by heating the dioxide with lanthanum and using the difference in boiling point between La (bp  $3457^\circ\text{C}$ ) and americium ( $2607^\circ\text{C}$ ) to displace the equilibrium to the right as americium distils.



Americium undergoes slow oxidation in air and dissolves in dil. HCl, as expected from its favourable potential [ $E(\text{Am}/\text{Am}^{3+}) = -2.07$  V].

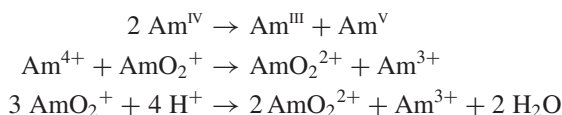
### 11.13.1 Potentials

The relevant standard potentials for americium (1M acid) are:



The tendency for the (+3) state to become more stable in the sequence  $\text{U} < \text{Np} < \text{Pu}$  continues with americium (and dihalides,  $\text{AmX}_2$ , make their appearance for the first time). The pink  $\text{Am}^{3+}$  ion is thus the most important species in aqueous solution,  $\text{Am}^{\text{IV}}$  being unstable in the absence of complexing agents. Hypochlorite oxidizes  $\text{Am}^{3+}$  in alkaline solution to what may be  $\text{Am}(\text{OH})_4$ , soluble in  $\text{NH}_4\text{F}$  solution, very likely as the fluoride complex  $[\text{AmF}_8]^{4-}$ . The (+5) state is accessible, again through oxidation in alkaline solution (e.g., with  $\text{O}_3$  or peroxydisulfate,  $\text{S}_2\text{O}_8^{2-}$ ), as the  $\text{AmO}_2^+$  ion, though this tends to disproportionate to  $\text{Am}^{\text{III}}$  and  $\text{Am}^{\text{V}}$ ; the (+6) state, in the form of the  $\text{AmO}_2^{2+}$  ion, is obtained by oxidation ( $\text{Ag}^{2+}$  or  $\text{S}_2\text{O}_8^{2-}$ ) of lower oxidation states in acid solution.

The tendency noted for plutonium for disproportionation occurs here, as both  $\text{Am}^{\text{IV}}$  and  $\text{Am}^{\text{V}}$  tend to disproportionate in solution:



There is also again the tendency to autoradiolysis, the reduction of high oxidation states through the effects of the  $\alpha$ -radiation emitted.

Relatively few complexes of americium have been characterized; those that have tend to resemble the corresponding compounds of the three previous metals. Many are halide complexes, such as  $(\text{NH}_4)_4 [\text{AmF}_8]$ , which resembles the U analogue,  $\text{Cs}_2\text{NaAmCl}_6$ , and  $(\text{Ph}_3\text{PH})_3\text{AmX}_6$  ( $\text{X} = \text{Cl}, \text{Br}$ ).

The  $\text{AmO}_2^+$  and  $\text{AmO}_2^{2+}$  ions form well-defined complexes; thus in HCl solution, where it likely forms  $[\text{AmO}_2\text{Cl}_4]^{3-}$  and  $[\text{AmO}_2\text{Cl}_4]^{2-}$ , the symmetric  $\text{Am}=\text{O}$  stretching vibrations can be detected at 730 ( $\text{AmO}_2^+$ ) and 796  $\text{cm}^{-1}$  ( $\text{AmO}_2^{2+}$ ), respectively.  $\text{Na}[\text{AmO}_2(\text{OAc})_3]$  has eight coordination with bidentate acetates, just like the U–Pu analogues, the same coordination number also being found in  $\text{AmO}_2\text{F}_2$ ,  $\text{M}[\text{AmO}_2\text{F}_2]$  ( $\text{M} = \text{Rb}, \text{K}$ ), and  $\text{M}[\text{AmO}_2\text{CO}_3]$  ( $\text{M} = \text{Rb}, \text{K}, \text{Cs}$ ). Six coordination occurs in  $\text{Cs}_2[\text{AmO}_2\text{Cl}_4]$  and in  $\text{NH}_4[\text{AmO}_2\text{PO}_4]$ .

A significant chemistry occurs in the (+3) state, similar to that of  $\text{Ln}^{3+}$  ions, with studies often made in the context of separating Am from lanthanide fission products. Amide ligands like *N, N, N', N'*-tetraethylmalonamide (TEMA) have been investigated as possible extractants. Solution studies are assisted by some of the newer spectroscopic techniques; thus EXAFS (Extended X-ray Absorption Fine Structure) studies on solutions of  $[\text{Am}(\text{TEMA})_2(\text{NO}_3)_3]$  indicate a similar geometry to  $[\text{Nd}(\text{TEMA})_2(\text{NO}_3)_3]$ . Carboxylate-derived calix[4]arenes show high selectivity for  $\text{Am}^{3+}$ , whilst complexation of  $\text{Am}^{3+}$  by crown ethers and diazacrown ethers has also been studied. The resemblance extends to complexes isolated. The sulfate  $\text{Am}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$  is isomorphous with the 8-coordinate lanthanide analogues (Pr–Sm) and insoluble oxalates  $\text{Am}_2(\text{C}_2\text{O}_4)_3 \cdot x \text{H}_2\text{O}$  ( $x = 7, 11$ ) have been characterized. The resemblance extends to diketonate complexes such as  $[\{\text{Am}(\text{Me}_3\text{CCOCHCOCHMe}_3)_3\}_2]$ , a dimer with seven-coordinate Am, like the Pr analogue. The adduct  $[\text{Am}(\text{CF}_3\text{CCOCHCOCCF}_3)_3\{(\text{BuO})_3\text{PO}\}_2]$  is volatile at 175 °C and potentially could be used in separations. In the iodate complex  $\text{K}_3\text{Am}_3(\text{IO}_3)_{12} \cdot \text{HIO}_3$ , the  $[\text{AmO}_8]$  polyhedra are made of eight  $[\text{IO}_3]$  oxygen atoms in a distorted bicapped trigonal prismatic array. There is additionally one very long Am–O contact to complete a distorted tricapped trigonal prismatic Am coordination sphere.

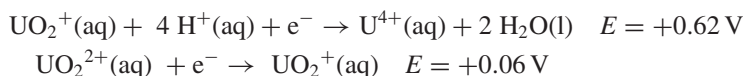
## 11.14 Chemistry of the Later Actinides

The succeeding actinides (Cm, Bk, Cf, Es, Fm, Md, No, Lr) mark the point where the list of isolated compounds tends to involve binary compounds (oxides, halides and halide complexes, chalcogenides, and pnictides) rather than complexes. Those studies of complexes that have been made are usually carried out in solution and, from Fm, onwards, have been tracer studies.

Fermium coprecipitates with lanthanide fluorides and hydroxides, showing it to form lanthanide-like  $\text{Fm}^{3+}$  ions. These elute from cation-exchange resins slightly before  $\text{Es}^{3+}$ , whilst its chloride and thiocyanate complexes are eluted from anionic exchange resins just

after  $\text{Es}^{3+}$ . This shows that  $\text{Fm}^{3+}$  forms slightly stronger complexes than does  $\text{Es}^{3+}$ , as expected purely on electrostatic considerations for a slightly smaller ion. In the case of nobelium, slightly different results have been obtained. Nobelium ions coprecipitate with  $\text{BaF}_2$ , rather than with  $\text{LaF}_3$ , suggesting that they are present as  $\text{No}^{2+}$  ions, but, after adding  $\text{Ce}^{4+}$  oxidant to the initial solution, nobelium precipitated with  $\text{LaF}_3$ , indicating that the cerium had oxidized the nobelium to  $\text{No}^{3+}$  ions. Complexing studies using  $\text{Cl}^-$  ions also indicated alkaline-earth-like behaviour.

**Question 11.1** Use the reduction potentials to show why the  $\text{UO}_2^+(\text{aq})$  tends to disproportionate.



**Answer 11.1** Combining the potentials shows that for



Since  $E$  is positive, the reaction is energetically feasible; although this only predicts that the  $\text{UO}_2^+(\text{aq})$  ion is *thermodynamically unstable* with respect to disproportionation and says nothing about *kinetic stability*, the fact is that the uranium(V) aqua ion is very short-lived.

**Question 11.2** Write the expression for  $K_1$  and  $K_2$  for complex formation between  $\text{Th}^{4+}$  and  $\text{F}^-$  ions.

**Answer 11.2**

$$K_1 = [\text{ThF}^{3+}(\text{aq})]/[\text{Th}^{4+}(\text{aq})][\text{F}^-(\text{aq})]; K_2 = [\text{ThF}_2^{2+}(\text{aq})]/[\text{ThF}^{3+}(\text{aq})][\text{F}^-(\text{aq})]$$

**Question 11.3** The highest occupied orbitals in the uranyl ion have the electronic arrangement  $\sigma_u^2 \sigma_g^2 \pi_u^4 \pi_g^4$ . By referring to Figure 11.2, suggest the electronic arrangements similarly of  $\text{UO}_2^+$  and  $\text{PuO}_2^{2+}$ .

**Answer 11.3**  $\text{UO}_2^+$  is  $\sigma_u^2 \sigma_g^2 \pi_u^4 \pi_g^4 (\delta_u, \phi_u)^1$  and  $\text{PuO}_2^{2+}$  is  $\sigma_u^2 \sigma_g^2 \pi_u^4 \pi_g^4 (\delta_u, \phi_u)^2$  (The relative positions of  $\delta_u$  and  $\phi_u$  are uncertain).

**Question 11.4** Suggest reasons why actinides from Cm onwards do not appear to form similar ions like  $\text{CmO}_2^{2+}$ .

**Answer 11.4** Heavier actinides such as Cm do not display high oxidation states as the f orbitals appear to be more contracted and their electrons are not available for bonding, (and could be required for  $\pi$  bonding, for example). A further factor is that the additional electrons would need to be placed in antibonding orbitals such as  $\sigma_u^*$  and  $\pi_u^*$ , which would destabilize such an ion.

**Question 11.5** Suggest coordination numbers for each of the following complexes. (a)  $[\text{UO}_2\text{F}_5]^{3-}$ ; (b)  $[\text{UO}_2\text{Br}_4]^{2-}$ ; (c)  $[\text{UO}_2(\text{NO}_3)_3]^-$ ; (d)  $[\text{UO}_2(\text{NCS})_5]^{3-}$ ; (e)  $[\text{UO}_2(\text{CH}_3\text{COO})_3]^-$ ; (f)  $[\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2]$ ; (g)  $[\text{UO}_2(\text{NO}_3)_2(\text{Ph}_3\text{PO})_2]$ ; (h)  $[\text{UO}_2(\text{CH}_3\text{COO})_2(\text{Ph}_3\text{PO})]$ .

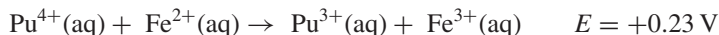
**Answer 11.5** (a) 7; (b) 6; (c) 8 (nitrate is bidentate) (d) 7; (e) 8 (acetate is bidentate) (f) 8; (g) 8; (h) 7.

**Question 11.6** Explain why you can get 2 + 6 coordination in  $[\text{UO}_2(\text{OH}_2)_2(\text{O}_2\text{NO})_2]$ ,  $[\text{UO}_2(\text{O}_2\text{NO})_3]^-$ , etc. rather than the 2 + 5 coordination in the uranyl aqua ion.

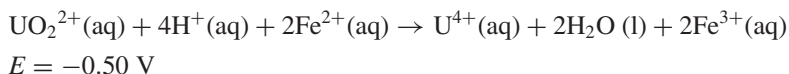
**Answer 11.6** Although bidentate in most complexes, nitrate groups take up little space (they are said to have a small ‘bite angle’).

**Question 11.7** Read section 11.5.5 and explain why  $\text{Pu}^{4+}$  can be reduced by  $\text{Fe}^{2+}$ , but  $\text{UO}_2^{2+}$  can’t be so reduced.

**Answer 11.7**  $\text{Fe}^{3+}(\text{aq})$  has a more negative reduction potential than  $\text{Pu}^{4+}(\text{aq})$ , making  $\text{Fe}^{2+}$  a better reducing agent, one that will reduce  $\text{Pu}^{4+}(\text{aq})$ . Thus for:



and the process is energetically feasible. However, for:

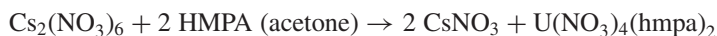


and the reduction is not energetically feasible under these conditions.

**Question 11.8** The infrared spectrum of  $\text{Th}(\text{NO}_3)_4 \cdot 4 \text{ Me}_3\text{PO}$  displays bands due to bidentate nitrate and ionic nitrate groups. Suggest a possible structure affording a reasonable coordination number.

**Answer 11.8** Phosphine oxide ligands and bidentate nitrate groups take up different amounts of space round thorium. Assuming that all the phosphine oxide groups are bound to thorium, reference to Table 11.5 suggests that a coordination number of 10 is likely; four  $\text{Me}_3\text{PO}$  groups bound would leave room for three bidentate nitrates. The suggested structure is  $[\text{Th}(\text{NO}_3)_3(\text{Me}_3\text{PO})_4]^+ \text{NO}_3^-$ .

**Question 11.9 (Refer to section 11.6.2 in connection with this)** Hexamethylphosphoramide (HMPA),  $\text{OP}(\text{NMe}_2)_3$ , is a good  $\sigma$ -donor, behaving like a typical monodentate phosphine oxide ligand such as  $\text{Ph}_3\text{PO}$ . A number of complexes of HMPA with uranium(IV) nitrate have been prepared. Green crystals of  $\text{U}(\text{NO}_3)_4(\text{hmpa})_2$  are made thus:



The IR spectrum of this compound shows only one type of nitrate group; all are coordinated.

**Question A** How are the nitrates likely to be bound in  $\text{U}(\text{NO}_3)_4(\text{hmpa})_2$ ? Suggest a coordination number and coordination geometry for uranium.

**Answer A** By analogy with  $\text{U}(\text{NO}_3)_4(\text{OPPh}_3)_2$ , a 10-coordinate compound with a *trans* geometry and bidentate nitrates is probable (*this is known to be the case*).

Using excess of HMPA, a green compound  $\text{U}(\text{NO}_3)_4(\text{hmpa})_4$  is obtained. Its IR spectrum shows two different modes of nitrate coordination, and no ionic nitrate.

**Question B** Suggest a credible structure for the compound  $\text{U}(\text{NO}_3)_4(\text{hmpa})_4$ , indicating the coordination number of uranium.

**Answer B** Various structures are possible. It is unlikely that all nitrates are bidentate, as this product would be 12 coordinate. If one nitrate is monodentate, the compound would be 11 coordinate  $\text{U}(\text{O}_2\text{NO})_3(\text{ONO}_2)(\text{hmpa})_4$ .



If  $\text{U}(\text{NO}_3)_4(\text{hmpa})_4$  is dissolved in non-polar solvents such as  $\text{CH}_3\text{CN}$ , a non-conducting solution is obtained, but with a simpler IR spectrum possibly indicating just one type of nitrate coordination.

**Question C** Suggest a structure for the compound present in solution.

**Answer C** One alternative is an 11-coordinate complex  $\text{U}(\text{NO}_3)_4(\text{hmpa})_3$  formed by dissociation of one hmpa ligand.

When  $\text{U}(\text{NO}_3)_4(\text{hmpa})_4$  is treated with  $\text{NaBPh}_4$ , a crystalline solid is obtained which has the analysis  $\text{U}(\text{NO}_3)_3(\text{hmpa})_4\text{BPh}_4$ . This is a 1:1 electrolyte in solution. Its IR spectrum shows only one type of nitrate group, and no ionic nitrate.

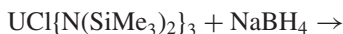
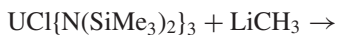
**Question D** Suggest a credible structure for this compound, indicating the coordination number of uranium.

**Answer D** Assuming all nitrates are bidentate and that the  $\text{BPh}_4^-$  group remains ionic, a structure  $[\text{U}(\text{NO}_3)_3(\text{hmpa})_4]^+(\text{BPh}_4)^-$  would contain 10-coordinate uranium.

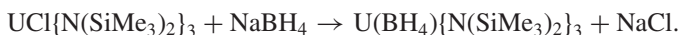
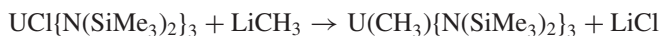
**Question 11.10** Comment on the patterns in bond length in Table 11.6.

**Answer 11.10** The U–X distances increase with increasing radius of halogen, as expected. There appears to be a slight decrease in U–O distance as the  $\sigma$ -donor power of the halogen decreases, possibly because this means that the ligands are competing for metal orbitals.

**Question 11.11** Complete these equations:



**Answer 11.11**







# 12 Electronic and Magnetic Properties of the Actinides

By the end of this chapter you should be able to:

- understand that the Russell–Saunders coupling scheme is not a good approximation here;
- recognize that the electronic spectra of compounds in the +3 and +4 states are dominated by f–f transitions;
- know that transitions are more sensitive to ligand than with the 4f metals;
- appreciate that interpretation of spectroscopic and magnetic properties is more difficult than for the lanthanides.

## 12.1 Introduction

In general, it is more difficult to interpret the spectra and magnetic behaviour of actinide compounds than those of lanthanide compounds, so this chapter will provide a qualitative and somewhat superficial discussion of the phenomena rather than a qualitative one, concentrating largely upon uranium compounds. The reasons for this is that spin–orbit coupling plays a more important part in actinide chemistry as the 5f orbitals and their electrons are not so ‘core-like’ as the 4f, particularly in the early part of the actinide series. This means that the Russell–Saunders (RS) coupling scheme, which treats spin–orbit coupling as being much weaker than interelectronic repulsion terms, is not applicable in most cases. Neither, however, can one usually apply the other extreme, the j–j coupling scheme, which relies on spin–orbit coupling being strong compared with electrostatic repulsion. Thus the ‘intermediate’ coupling scheme (intermediate between RS and jj) is used. It will be recalled that the f–f electronic transitions in the spectra of lanthanide complexes are relatively weak in comparison with those of transition metal complexes. However, in the case of the actinides, the 5f orbitals are larger than lanthanide 4f orbitals, so that they interact more with ligand orbitals, causing much higher extinction coefficients and also, because covalency is greater, to create greater nephelauxetic effects in actinide spectra. This means that there is more variation in both position and intensity of absorption bands than in lanthanide compounds. The ‘forbidden’ electronic dipole transitions are allowed in the presence of an asymmetric ligand field, which can arise by either a permanent distortion or by temporary coupling with an asymmetric metal–ligand vibration (vibronic coupling). Apart from the f–f transitions, there are two more types of absorption bands to note in actinide spectra. In general, the parity-allowed 5f–6d transitions occur above  $20\,000\text{ cm}^{-1}$ , since the 6d levels are considerably above 5f for most actinides; these are more intense (and broader) than the f–f

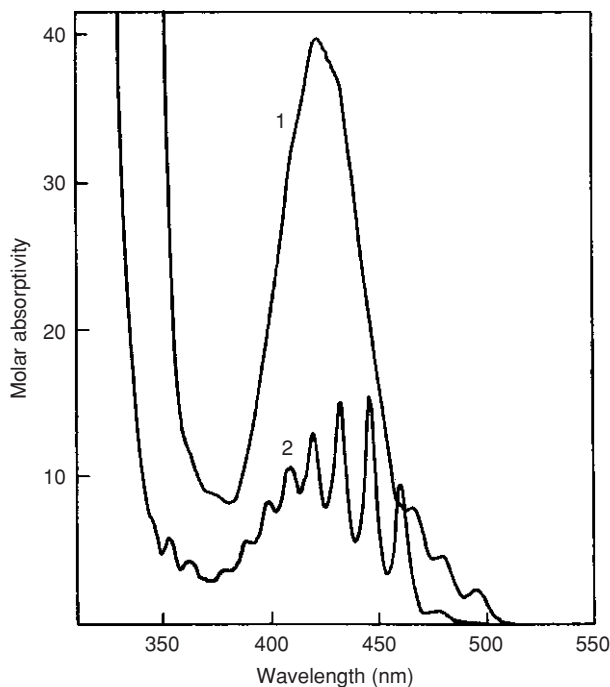
transitions. In the case of the free  $U^{3+}$  ion, the  $5f^26d^1$  level is over  $30\,000\text{ cm}^{-1}$  above the  $5f^3$  ground state, while in  $U^{3+}(\text{aq})$  the charge-transfer transitions start around  $24\,000\text{ cm}^{-1}$ ; solvation thus has a very significant effect upon the relative energies of the  $5f$  and  $6d$  electrons. Metal–ligand charge-transfer transitions have their maxima out in the ultraviolet, but, as with transition metals, the tail of these broad and often very intense absorption bands runs into the visible region of the spectrum, and is responsible for the red, brown, or yellow colours often noted for actinide complexes with polarizable ligands like Br or I.

## 12.2 Absorption Spectra

### 12.2.1 Uranium(VI) – $UO_2^{2+} - f^0$

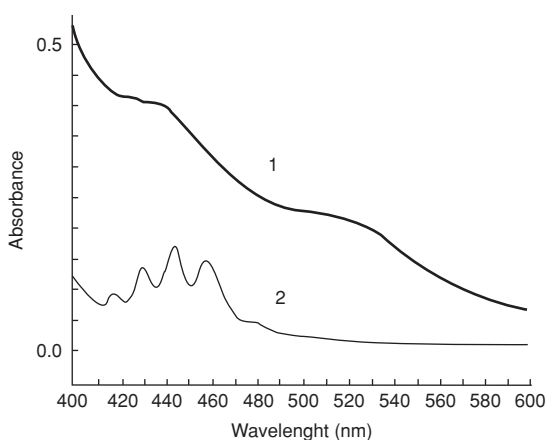
The ground state of the uranyl ion has a closed-shell electron configuration. There is a characteristic absorption  $\sim 25\,000\text{ cm}^{-1}$  (400 nm) which frequently gives uranyl compounds a yellow colour (though other colours like orange and red are not infrequent). This absorption band often exhibits fine structure due to progressions in symmetric  $O=U=O$  vibrations in the excited state, sometimes very well resolved, sometimes not (Figures 12.1 and 12.2).

It should also be remarked that uranyl complexes tend to emit a bright green fluorescence under UV irradiation, from the first excited state. This is used by geologists both to identify and to assay uranium-bearing minerals in deposits of uranium ores.



**Figure 12.1**

The absorption spectrum of (1)  $[UO_2(OAc)_4]^{2-}$  in liquid  $Et_4NOAc \cdot H_2O$ , showing the lack of vibronic structure, due to hydrogen bonding; (2)  $[UO_2(OAc)_3]^-$  in MeCN solution, showing the progression due to the  $O=U=O$  stretching vibration (from J.L. Ryan and W.E. Keder, *Adv. Chem. Ser.*, 1967, **71**, 335 and reproduced by permission of the American Chemical Society).



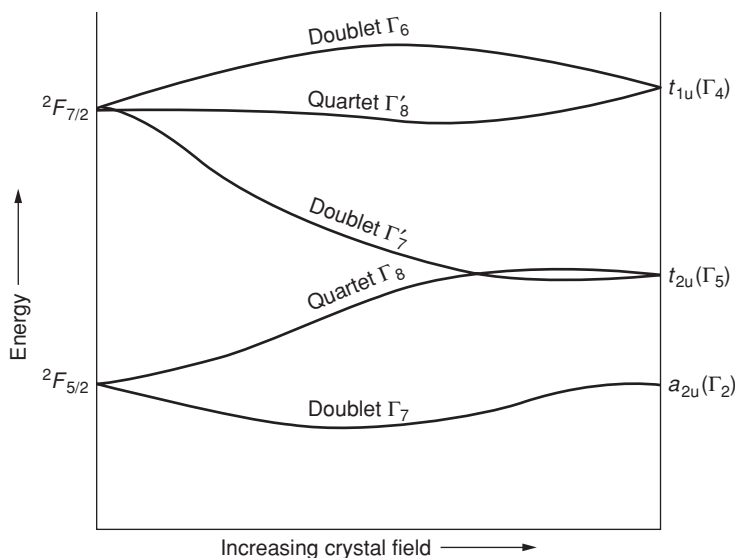
**Figure 12.2**

Absorption spectra of THF solutions of 1  $[\text{UO}_2\text{Cl}\{\eta^3\text{-CH}(\text{Ph}_2\text{PNSiMe}_3)_2\}(\text{thf})]$  and 2  $[\text{UO}_2\text{Cl}\{\eta^3\text{-N}(\text{Ph}_2\text{PNSiMe}_3)_2\}(\text{thf})]$  (reproduced with permission of the Royal Society of Chemistry from M.J. Sarsfield, H. Steele, M. Helliwell, and S.J. Teat, *Dalton Trans.*, 2004, 3443).

### 12.2.2 Uranium(v) – $f^1$

The  $^2F$  ground state is split into two levels,  $^2F_{7/2}$  and  $^2F_{5/2}$ , by spin–orbit coupling in the free ion. These are split further under the influence of a crystal field; the effect on the energy levels of increasing the crystal field up to the strong field limit is shown in Figure 12.3.

Four transitions are thus expected in the electronic spectrum and generally, in practice, four groups of lines are seen, between the near-IR and the visible, bearing out this prediction. The ground state is a Kramers' doublet ( $\Gamma_7$ ), so  $\text{U}^{\text{V}}$  compounds are EPR active.



**Figure 12.3**

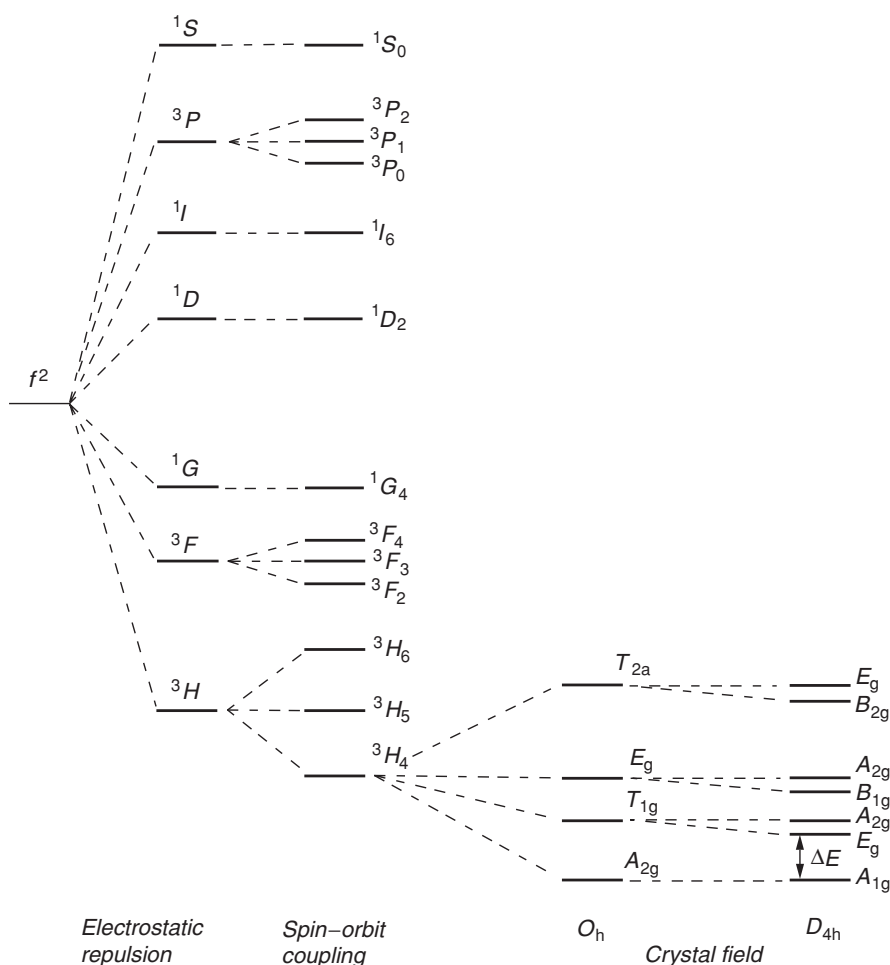
The effect of increasing crystal field upon the energy of an electron in an  $f^1$  system such as  $\text{U}^{\text{V}}$  (reproduced with permission from S.A. Cotton. *Lanthanides and Actinides*, Macmillan, 1991, p. 109).

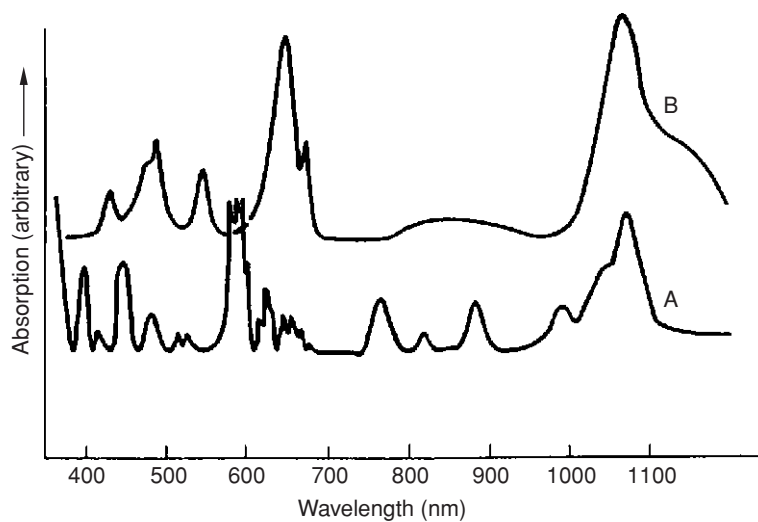
### 12.2.3 Uranium(IV) – $f^2$

The ground state arising from the  $f^2$  configuration is  $^3H_4$  (Figure 12.4) and the effect of a crystal field is to split both that and excited states further. A large number of electronic transitions are thus expected, and this is borne out in practice (Figures 12.5 and 12.6).

It will be noted that the transitions are often broader than those found in the spectra of lanthanide complexes – and indeed the later actinides, see Section 12.2.4. The 5f energy levels are more sensitive to coordination number than are the corresponding levels in the lanthanides; since there are bigger crystal-field effects, one sees pronounced differences between the spectra of 6-coordinate  $[UCl_6]^{2-}$  and of  $U^{4+}(aq)$  (Figure 12.5), leading to the conclusion that the uranium(IV) aqua ion was not six coordinate (most recent EXAFS results suggest a value of 9 or 10, see Table 11.1). Figure 12.6 displays another example of the difference in spectra between similar complexes of different coordination number.

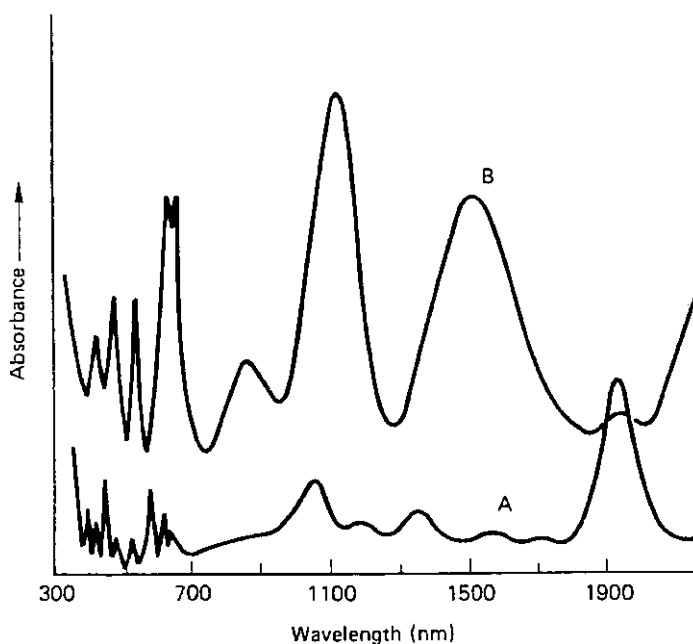
**Figure 12.4**  
A qualitative energy-level diagram for the  $U^{4+}$  ion, showing successively the effects of electrostatic repulsion, spin-orbit coupling, and crystal-field splitting (the latter shown only for the ground state). Overlap between levels is neglected. Adapted from M. Hirose *et al.*, *Inorg. Chim. Acta*, 1988, **150**, L93, and reproduced by permission of the Editor.





**Figure 12.5**

The absorption spectra of octahedral  $[\text{UCl}_6]^{2-}$  (A) and 9–10-coordinate  $\text{U}^{4+}(\text{aq})$  (B) (redrawn from D.M. Gruen and R.L. Macbeth, *J. Inorg. Nucl. Chem.*, 1959, **9**, 297 and reproduced by permission of Elsevier Science Publishers).



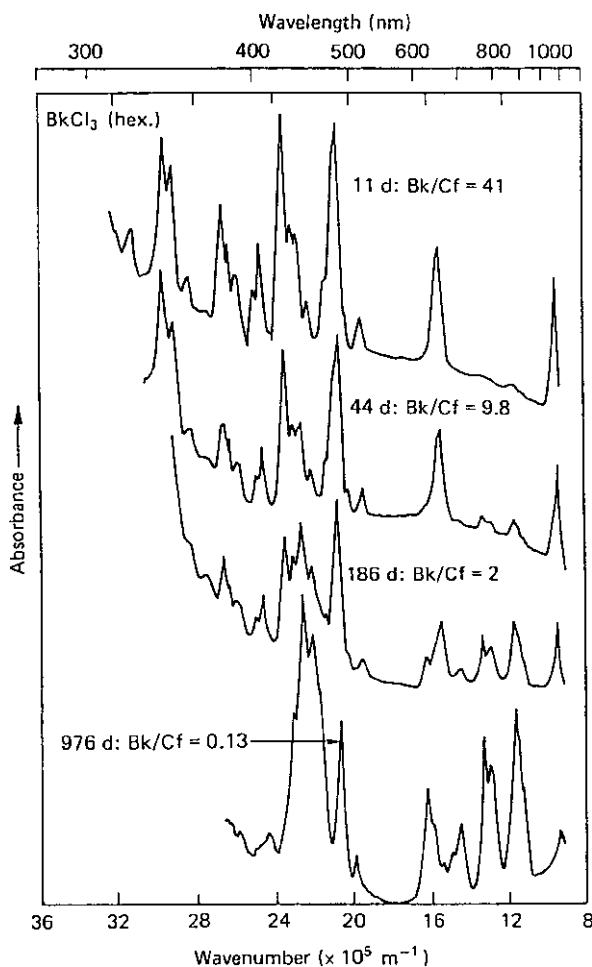
**Figure 12.6**

Solid-state absorption spectra of octahedral  $[\text{UCl}_4(\text{Bu}^t\text{SO})_2]$  (A) and 8-coordinate  $[\text{U}(\text{Me}_2\text{SO})_2] \text{I}_4$  (B) (redrawn from J.G.H. DuPreez and B. Zeelie, *Inorg. Chim. Acta*, 1989, **161**, 187 and reproduced by permission of Elsevier Science Publishers).

Detailed investigations have been made of the octahedral  $[\text{UCl}_6]^{2-}$  ion. Its spectrum is largely vibronic in nature, with electronic transitions accompanied by vibrations of the complex ion (odd-parity modes – the  $T_{1u}$  asymmetric stretch and  $T_{1u}$  and  $T_{2u}$  deformations). Here, as in other  $\text{U}^{\text{IV}}$  cases, overlap of bands from different states occurs because of the similarity in crystal-field and spin-orbit coupling effects. Its spectrum can be altered by destroying the centre of symmetry (e.g., by hydrogen bonding), which enables pure electronic transitions to be observed, and alters band patterns in multiplets.

### 12.2.4 Spectra of the Later Actinides

Because of the relatively short half-lives of many later actinides, purity of samples and correct identification of lines can be a matter of uncertainty, but Figure 12.7 shows how this

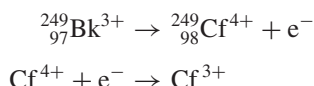


**Figure 12.7**

The absorption spectrum of the hexagonal form of  $\text{BkCl}_3$  as a function of time. The changes in the spectrum are due to the formation of  $\text{CfCl}_3$ . Note the sharp 'lanthanide-like' transitions characteristic of the later actinide (+3) state. (from J.R. Peterson *et al.*, *Inorg. Chem.*, 1986, **25**, 3779 reproduced by permission of the American Chemical Society).

can be turned to advantage. It shows spectra obtained over a period of time from a sample of  $^{249}\text{BkCl}_3$  beginning 11 days after synthesis. Now,  $^{249}\text{Bk}$  is a  $\beta$ -emitter with a half-life of 320 days, and the spectrum obtained over a 976 day period (three half-lives, during which time the berkelium decays to some 12.5 % of its original amount) shows the loss of the characteristic absorptions due to the  $^{249}\text{BkCl}_3$  and their replacement by a spectrum due to  $^{249}\text{CfCl}_3$ . These spectra are very reminiscent of the sharp, line-like absorptions obtained from the lanthanides. This reflects the fact that chemically the heavy actinides are lanthanide-like, suggesting that with increasing atomic number the 5f orbitals are now more core-like and thus less readily influenced by environment.

After the emission of a  $\beta$ -particle from the Bk nucleus the californium ion regains an electron to maintain the (+ 3) oxidation state:



It may also be noted that crystal type is retained; X-ray diffraction confirms that the  $\text{CfCl}_3$  retains the hexagonal structure of the original  $\text{BkCl}_3$  rather than adopting the orthorhombic modification.

## 12.3 Magnetic Properties

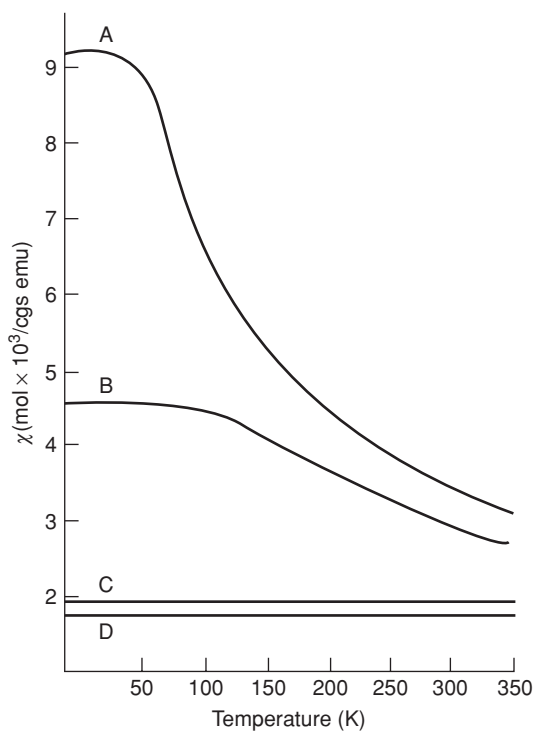
Uranium(VI) compounds are expected to be diamagnetic, with their  $^1\text{S}_0$  ( $f^0$ ) ground state. However, compounds like  $\text{UF}_6$  and uranyl complexes in fact exhibit temperature-independent paramagnetism, explained by a coupling of paramagnetic excited states with the ground state.

Uranium(V) compounds are, as expected for an  $f^1$  system, paramagnetic, usually exhibiting Curie–Weiss behaviour, with large Weiss constants;  $g$ -values, expected to be 6/7, are modified by the mixing in of higher states and by orbital-reduction effects (covalency), experimental  $g$ -values including values of 1.2 in  $\text{Na}_3\text{UF}_8$  and 0.71 in  $\text{CsUF}_6$ .

Matters are more complicated for uranium(IV); this  $f^2$  system has a  $^3\text{H}_4$  ground state, the energy level diagram has already been given (Figure 12.4). In a regular octahedral geometry, there is no contribution to the paramagnetic susceptibility from the first-order Zeeman term. Species like the  $[\text{UCl}_6]^{2-}$  ion (and isoelectronic  $\text{PuF}_6$ ) display temperature-independent paramagnetism, caused by the second-order Zeeman term mixing the  $^3\text{T}_{1g}$  excited state into the ground state. In lower symmetry, such as a  $D_{4h}$  *trans*- $\text{UX}_4\text{L}_2$  complex, both the first- and second-order Zeeman effects contribute to the susceptibility. If there is a small distortion from a regular octahedron, the splitting of the  $^3\text{T}_{1g}$  excited state is small, so that  $\Delta E$  in Figure 12.4 is large. There is thus little thermal population of these excited states, so the first-order Zeeman effect is small; the paramagnetic susceptibility shows little or no temperature dependence. As the distortion becomes larger, in complexes like  $\text{UBr}_4(\text{Et}_3\text{AsO})_2$  and  $\text{UI}_4[(\text{Me}_2\text{N})_3\text{PO}]_2$ , thermal population of a component of the  $^3\text{T}_{1g}$  excited state becomes more feasible, and thus the susceptibility shows a greater temperature dependence. In the case of a *cis*- $\text{UX}_4\text{L}_2$  complex, with  $D_{4h}$  symmetry, there is no first-order Zeeman term, so that the second-order Zeeman effect causes temperature-independent paramagnetism.

Figure 12.8 shows variable-temperature susceptibility data for some  $\text{U}^{\text{IV}}$  complexes of these types, which is in keeping with these explanations.



**Figure 12.8**

Temperature dependence of the magnetic susceptibility of some uranium(IV) complexes: (A) *trans*-[UBr<sub>4</sub>(Et<sub>3</sub>AsO)<sub>2</sub>]; (B) *trans*-[UCl<sub>4</sub>(Et<sub>3</sub>AsO)<sub>2</sub>]; (C) (Ph<sub>4</sub>P)<sub>2</sub> [UCl<sub>6</sub>]; (D) *cis*-[UCl<sub>4</sub>(Ph<sub>3</sub>PO)<sub>2</sub>] (redrawn from B.C. Lane and L.M. Venanzi, *Inorg. Chim. Acta*, 1969, **3**, 239 and reproduced by permission of the editor).

Few data are available for uranium(III) compounds, but a number of compounds with the  $f^3$  configuration, like Cs<sub>2</sub>NaUCl<sub>6</sub>, have  $\mu \sim 3.2 \mu_B$ , which is largely temperature independent.

# 13 Organometallic Chemistry of the Actinides

By the end of this chapter you should be able to:

- recall that these compounds are very air- and water-sensitive;
- recall that the bonding has a significant polar character, especially in the +3 state, but that +4 compounds, especially those of uranium, have more stability;
- recall that these compounds usually have small molecular structures with appropriate volatility and solubility properties;
- recall appropriate bonding modes for the organic groups;
- suggest suitable synthetic routes;
- suggest structures for suitable examples;
- appreciate the contribution of the  $C_5Me_5$  ligand in uranium chemistry;
- recall the unique properties of uranocene;
- appreciate the unusual compounds that can be made using imide and CO as ligands.

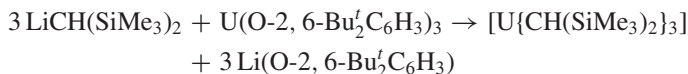
## 13.1 Introduction

Although lacking  $\pi$ -bonded compounds in low oxidation states that characterize the d-block elements, the actinides have a rich organometallic chemistry. Their compounds frequently exhibit considerable thermal stability, but like the lanthanide compounds are usually intensely air- and moisture-sensitive. They are often soluble in aromatic hydrocarbons such as toluene and in ethers (e.g., THF) but are generally destroyed by water. Sometimes they are pyrophoric on exposure to air. Most of the synthetic work has been carried out with Th and U; this is partly due to the ready availability of  $MCl_4$  ( $M = Th, U$ ) and also because of the precautions that have to be taken in handling compounds of other metals, especially Pu and Np.

## 13.2 Simple $\sigma$ -Bonded Organometallics

During the Manhattan project, a wide range of compounds was screened in the search for volatile uranium compounds that could be used for separation of isotopes of uranium, since  $UF_6$  was not an easy compound to handle. The leading organometallic chemist of the day, Henry Gilman, investigated the synthesis of simple alkyls and aryls, concluding that such compounds did not exist, or at least were unstable. Even today, just one neutral homoleptic

alkyl of known structure exists,  $[\text{U}\{\text{CH}(\text{SiMe}_3)_2\}_3]$ , made from an aryloxide by a route ensuring no contamination with lithium halide:

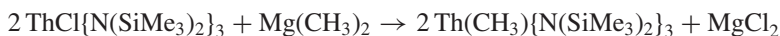
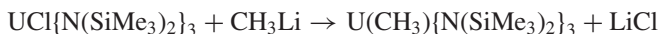


If  $\text{LiCH}(\text{SiMe}_3)_2$  is treated directly with  $\text{UCl}_3(\text{THF})_3$  in a salt-elimination reaction the alkylate salt  $[(\text{THF})_3\text{Li-Cl-U}\{\text{CH}(\text{SiMe}_3)_2\}_3]$  is obtained.

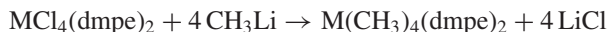
$[\text{U}\{\text{CH}(\text{SiMe}_3)_2\}_3]$  has a trigonal pyramidal structure, like the corresponding lanthanide alkyls (Section 6.2.1) and also like the isoelectronic amides  $[\text{M}\{\text{N}(\text{SiMe}_3)_2\}_3]$  ( $\text{M} = \text{U}$ , lanthanides). There are some agostic  $\text{U} \cdots \text{H}-\text{C}$  interactions. Similar Np and Pu compounds  $[\text{M}\{\text{CH}(\text{SiMe}_3)_2\}_3]$  have been made. *Ab initio* MO calculations for hypothetical  $\text{M}(\text{CH}_3)_3$  ( $\text{M} = \text{U}$ , Np, Pu) molecules also predict pyramidal structures as a result of better 6d involvement (*not 5f*) in the  $\text{M}-\text{C}$  bonding orbitals in pyramidal geometries.

The benzyl  $[\text{Th}(\text{CH}_2\text{Ph})_4]$  has been synthesized and the pale yellow dimethylbenzyl compound  $\text{Th}(1,3,5\text{-CH}_2\text{C}_6\text{H}_3\text{Me}_2)_4$  has also been reported, but their structures are not known (and may have multihapto-coordination of benzyl to thorium). The heptamethylthorate anion  $[\text{ThMe}_7]^{3-}$  is found in the salt  $[\text{Li}(\text{tmeda})]_3[\text{ThMe}_7]$  ( $\text{tmeda} = \text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2$ ). The latter contains thorium in monocapped trigonal prismatic coordination; one methyl is terminal ( $\text{Th}-\text{C}$  2.571 Å) whilst the other six methyl groups pairwise bridge the lithium and thorium ( $\text{Th}-\text{C}$  2.655–2.765 Å). The methyl groups are, however, equivalent in solution (NMR).

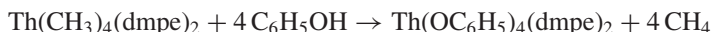
Certain simple alkyls are stabilized by the presence of either phosphine or amide ligands, thus:



These are pentane-soluble, volatile tetrahedral molecules. They have an extensive chemistry involving metallacycles which will be dealt with later (Section 13.6). Although  $\text{MMe}_4$  ( $\text{M} = \text{Th}$ , U) have not been isolated, this unit can be stabilized as eight-coordinate phosphine adducts, where the role of phosphines is to saturate the coordination sphere. The coordination of a 'soft' phosphine ligand to a 'hard' metal ion like uranium(IV) is noteworthy.



These react with phenol forming phenoxides:



Similar compounds  $[\text{M}(\text{CH}_2\text{Ph})_4(\text{dmpe})_2]$  (stable to 85 °C in the absence of air) and  $[\text{M}(\text{CH}_2\text{Ph})_3\text{Me}(\text{dmpe})_2]$  have been isolated; structures of  $[\text{Th}(\text{CH}_2\text{Ph})_4(\text{dmpe})_2]$  and  $[\text{U}(\text{CH}_2\text{Ph})_3\text{Me}(\text{dmpe})_2]$  confirm their identity, they have short  $\text{M}-\text{C}$  contacts. Compounds of alkyl groups like  $\text{CH}_2\text{CH}_3$  that are capable of undergoing elimination have not been isolated.

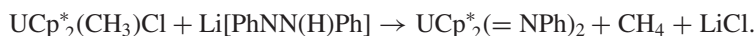
Compounds containing one or more cyclopentadienyl-type ligands are much more robust. (Throughout this section,  $\text{C}_5\text{H}_5$  is abbreviated to Cp;  $\text{C}_5\text{Me}_5$  is abbreviated to Cp\*;  $\text{C}_5\text{H}_4\cdot\text{CH}_3$  is MeCp.)

### 13.3 Cyclopentadienyls

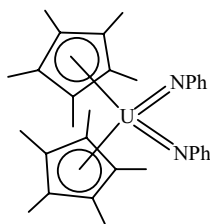
These are regarded as derivatives of the  $C_5H_5^-$  ligand; substituted rings also occur. Some of these were the first organoactinide compounds to be reported, shortly after the discovery of ferrocene. The most important compounds are in the +4 state but there is a significant chemistry of U(+3) as well as examples in oxidation states (+5) and (+6). One factor that should be noted is that replacing one or more hydrogens in the cyclopentadienyl ring can have a significant effect upon the stability and isolability of complexes made from them, through both steric and electronic effects. Thus three or four Cp ligands can be accommodated around uranium(IV), whereas with  $Cp^*$  two is the norm. In another example,  $[UCp_3]$  gives no sign of reacting with carbon monoxide;  $[U\{C_5H_3(SiMe_3)_2\}_3]$  forms a compound that can be detected in solution; and  $[U(C_5Me_4H)_3]$  forms  $[U(C_5Me_4H)_3(CO)]$ , which can be isolated in the solid state.

#### 13.3.1 Oxidation State (vi)

High oxidation states are not normally associated with organometallic chemistry, but a remarkable uranium(VI) imide has been made (Figure 13.1):



The reaction may go via an intermediate  $[UCp^*_2(\eta^2\text{-PhN-NPh})]$ . There are no f–f transitions in the visible spectrum, confirming its  $U^{VI}\text{-}f^0$  character, whilst the structure of this remarkable compound shows the expected pseudotetrahedral geometry; the short U–N bond length (1.952 Å) confirms its multiple-bond character and the  $U=N\text{-}Ph$  linkage is virtually linear.



**Figure 13.1**  
A uranium(VI) imide.

#### 13.3.2 Oxidation State (v)

Rare organoimides  $U(MeCp)_3(=NR)$  have been made by oxidation of  $U(MeCp)_3(thf)$  with  $RN_3$  ( $R = Me_3Si$  and  $Ph$ ). The U–N bond length of 2.109 Å is regarded as having multiple-bond character (cf. the U=O bond in uranyl compounds).

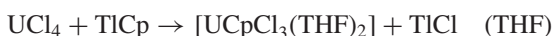
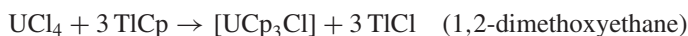


#### 13.3.3 Oxidation State (iv)

There are three families of compounds whose structures can be regarded as derived from a tetrahedral  $UX_4$  molecule with one or more halogens replaced by one or more

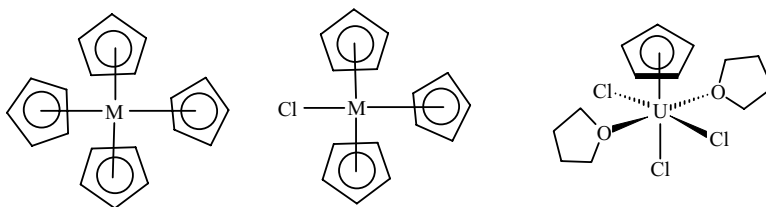
cyclopentadienyl rings;  $[\text{Cp}_4\text{An}]$ ,  $[\text{Cp}_3\text{AnX}]$ ;  $[\text{CpAnX}_3]$  ( $\text{X}$  = halogen, most usually Cl). Since halogens have less steric influence than a cyclopentadienyl group, a  $\text{CpAnX}_3$  molecule would be coordinatively unsaturated, so  $\text{CpAnX}_3$  actually exist as solvates like  $\text{CpAnX}_3(\text{THF})_2$ .  $\text{Cp}_2\text{AnX}_2$  are unknown for  $\text{X}$  = halogen, attempts to prepare them resulting in mixtures of  $[\text{Cp}_3\text{AnX}]$  and  $[\text{CpAnX}_3]$ , but they are known for  $\text{X} = \text{NEt}_2$  and  $\text{BH}_4$ .

### Syntheses



Some similar compounds can be made with other actinides, namely  $[\text{MCp}_4]$  ( $\text{M} = \text{Th}, \text{Pa}, \text{Np}$ ),  $[\text{MCp}_3\text{Cl}]$  ( $\text{M} = \text{Th}, \text{Np}$ ), and  $[\text{ThCpCl}_3]$ .

Sometimes other starting materials are used:



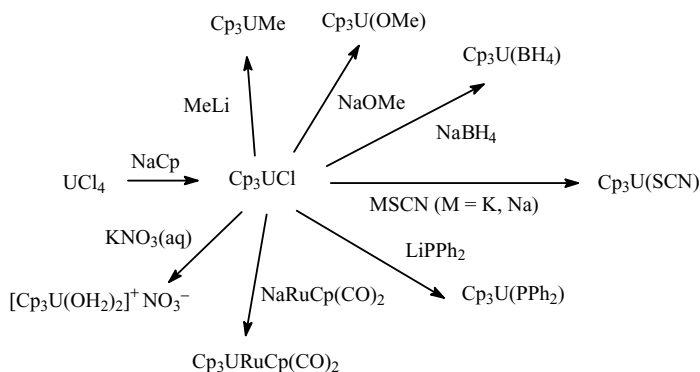
**Figure 13.2**

Structures of  $\text{MCp}_4$ ,  $\text{MCp}_3\text{Cl}$  and  $\text{MCpCl}_3(\text{THF})_2$ .

### Structures

$[\text{MCp}_4]$  have regular tetrahedral structures whilst  $[\text{MCp}_3\text{Cl}]$  are analogous (Figure 13.2) with the halogen occupying a position corresponding to the centroid of a fourth ring and  $[\text{UCpCl}_3(\text{thf})_2]$  has a pseudo-octahedral structure.

$[\text{MCp}_3\text{Cl}]$  are the most useful of these compounds as the halogen can be replaced by a number of groups (e.g.,  $\text{NCS}$ ,  $\text{BH}_4$ ,  $\text{acac}$ ,  $\text{Me}$ ,  $\text{Ph}$ ) (Fig. 13.3).

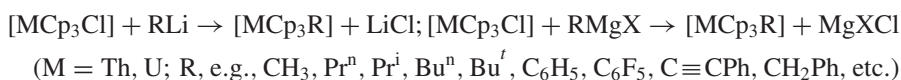


**Figure 13.3**

Synthesis and reactions of  $\text{Cp}_3\text{UCl}$ .

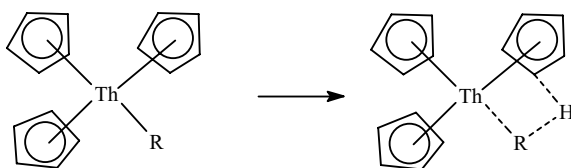
There is evidence for a significant covalent contribution to the bonding in some of these actinide(IV) compounds;  $\text{UCp}_3\text{Cl}$  does not react with  $\text{FeCl}_2$  forming ferrocene, whereas  $\text{MCp}_3$  do (M, e.g., Ln, U). It appears to undergo ionization in aqueous solution as a stable green  $[\text{UCp}_3(\text{OH}_2)_n]^+$  ( $n \sim 2$ ) cation. There is also some evidence from Mössbauer spectra of neptunium-(III) and -(IV) cyclopentadienyl compounds that in a  $\text{Np}^{\text{IV}}$  compound such as  $\text{NpCp}_4$  (but not  $\text{Np}^{\text{III}}$  compounds) there is a greater shielding of the 6s shell than in an ionic compound like  $\text{NpCl}_4$ , leading to enhanced covalence in the bond. Bonds are reasonably strong; the mean bond dissociation energy in  $\text{UCp}_4$  has been determined to be  $247 \text{ kJ mol}^{-1}$ , compared with a value of  $297 \text{ kJ mol}^{-1}$  for  $\text{FeCp}_2$ .

The most interesting  $[\text{MCp}_3\text{X}]$  compounds are the alkyls and aryls,  $[\text{MCp}_3\text{R}]$  being made by reaction with either organolithium compounds or Grignard reagents.



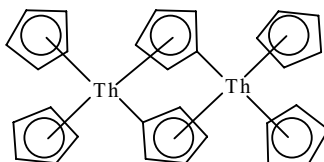
They were independently synthesized by three independent research groups at the start of the 1970s and represent the first compounds to have well-defined actinide-carbon  $\sigma$  bonds (structures for  $\text{M} = \text{U}$ ; R, e.g., Bu,  $\text{CH}_2\text{C}_6\text{H}_4\text{CH}_3$ , etc). (See, e.g., the papers by T.J. Marks group in *J. Am. Chem. Soc.*, 1973, **95**, 5529; 1976, **98**, 703.) Thermally stable *in vacuo*, they react with methanol, forming  $\text{MCp}_3(\text{OMe})$  and RH. A low-temperature NMR study of  $[\text{UCp}_3\text{Pr}^i]$  indicates restricted rotation about the U–C  $\sigma$  bond at low temperatures.

Bond disruption energies of 315–375 kJ/mol for the Th–C bonds in  $[\text{ThCp}_3\text{R}]$  (R, e.g.,  $\text{CH}_3$ ,  $\text{CH}_2\text{Ph}$ ) indicate the thermodynamic stability of these compounds, comparable with transition metal alkyls (the bond energies are 10–30 kJ/mol less for the uranium compounds). Decomposition does not occur by the  $\beta$ -elimination route; instead intermolecular abstraction of a hydrogen from a Cp ligand occurs (Figure 13.4) forming RH. A stable compound  $[\text{Cp}_2\text{Th}(\mu\text{-C}_5\text{H}_4)_2\text{ThCp}_2]$  is the other product (Figure 13.5).

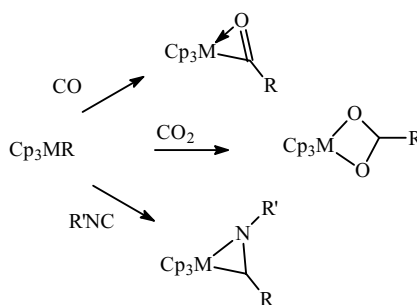


**Figure 13.4**  
Decomposition of  $\text{ThCp}_3\text{R}$ .

These compounds also undergo insertion reactions of CO,  $\text{CO}_2$ , and  $\text{R}'\text{NC}$  into the M–C sigma bond, forming  $[\text{Cp}_3\text{M}(\eta^2\text{-COR})]$ ,  $[\text{Cp}_3\text{M}(\eta^2\text{-O}_2\text{CR})]$ , and  $[\text{Cp}_3\text{M}(\eta^2\text{-C(R)NR}')]$ , respectively (Figure 13.6).

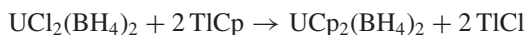
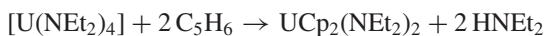


**Figure 13.5**  
Structure of  $[\text{Cp}_2\text{Th}(\mu\text{-C}_5\text{H}_4)_2\text{ThCp}_2]$ .

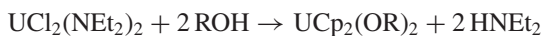


**Figure 13.6**  
Insertion reactions of  $\text{Cp}_3\text{MR}$ .

As already mentioned, there is no  $\text{UCp}_2\text{Cl}_2$  – attempts to make it giving mixtures of  $[\text{UCp}_3\text{Cl}]$  and  $[\text{UCpCl}_3]$ , but some  $\text{UCp}_2\text{X}_2$  can be made for example:



$\text{UCp}_2(\text{NEt}_2)_2$  reacts with  $\text{ROH}$  [ $\text{R}$  = bulky group, e.g.,  $(\text{Bu}^t)_3\text{C}$ ; 2,6- $\text{Me}_2\text{C}_6\text{H}_3$ ]:



### 13.3.4 Oxidation State (III)

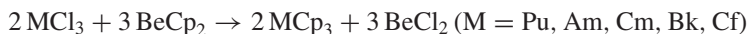
A variety of syntheses are possible to these compounds, including the expected salt-elimination route:



Reduction with sodium naphthalenide is often possible:



An unusual route used for several of the transuranium elements is a microscale reaction of the metal trichlorides with molten  $\text{BeCp}_2$  at  $65^\circ\text{C}$ .

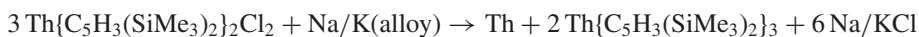


The cyclopentadienyl products were sublimed out of the reaction mixture and characterized by powder diffraction data, showing they were isostructural with the corresponding  $\text{LnCp}_3$  ( $\text{Ln} = \text{Pr, Sm, Gd}$ ).

Similar compounds have been made with substituted cyclopentadienyl groups; their properties strongly resemble those of the corresponding  $\text{LnCp}_3$ . The unsolvated  $\text{U}(\text{C}_5\text{H}_4\text{SiMe}_3)_3$  is known to have trigonal planar geometry, as is  $\text{U}(\text{C}_5\text{Me}_4\text{H})_3$  (X-ray). Lewis bases, e.g. THF,  $\text{C}_6\text{H}_{11}\text{NC}$ , py, form pseudotetrahedral adducts  $\text{UCp}_3\cdot\text{L}$  {X-ray, e.g. for  $[\text{UCp}_3(\text{THF})]$ } in the same way that lanthanides do. Some adducts are known with rather soft bases like tertiary phosphines, e.g.  $[\text{U}(\text{MeCp})_3(\text{PMe}_3)]$ , that might not have been expected for a fairly ‘hard’ metal such as  $\text{U}^{\text{III}}$ .

Evidence from UV–visible spectra (Cm and Am compounds) and Mossbauer spectra (Np compounds) indicates that these compounds have probably rather more covalent contributions to their bonding than do the corresponding lanthanide compounds, but are largely ionic compared with cyclopentadienyls in the +4 state.

Analogous compounds  $AnCp_3$  exist for other actinides, e.g. Th, Np (?), Pu, Am, Bk, Cf, Cm. The thorium(III) compound is especially noteworthy, on account of the rarity of this oxidation state; the structure of the similar  $Th\{C_5H_3(SiMe_3)_2\}_3$  is known to have trigonal planar geometry around thorium.

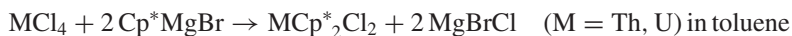


These  $Th^{III}$  compounds are EPR-active; spectra indicate a  $6d^1$  ground state for  $Th\{C_5H_3(SiMe_3)_2\}_3$ , despite the fact that the free  $Th^{3+}$  ion has a  $5f^1$  configuration.

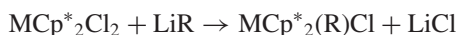
## 13.4 Compounds of the Pentamethylcyclopentadienyl Ligand ( $C_5Me_5 = Cp^*$ )

### 13.4.1 Oxidation State(IV)

Compounds of the type  $[MCp^*_2X_2]$  ( $M = Th, U$ ) are rather important. They owe their importance to the fact that although three  $Cp^*$  rings can be accommodated round uranium in  $UCp^*_3Cl$ , this compound cannot be made by direct synthesis (nor can  $MCp^*_3$ ), partly owing to the bulk of the  $C_5Me_5$  ligands, and the  $[MCp^*_2X_2]$  systems are in practice more readily obtained.



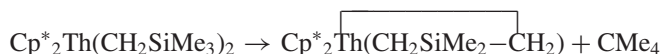
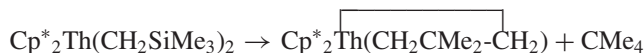
Halides can be replaced by suitable ligands, thus reactions with NaOMe and  $LiNMe_2$  afford products like  $ThCp^*_2(OMe)_2$ ,  $ThCp^*_2Cl(NMe_2)$ , and  $ThCp^*_2(NMe_2)_2$ .  $Li_2S_5$  reacts forming  $[ThCp^*_2(S_5)]$ . Importantly, the chloride compounds can be alkylated and arylated. Either one or two chlorines can be replaced.



They have the usual pseudotetrahedral coordination; the structure of  $Cp^*_2Th(CH_2CMe_3)_2$  reveals agostic  $Th \cdots H-C$  interactions with the  $\alpha-C-H$  bonds. The  $M-C$   $\sigma$  bonds seem to have a significant ionic contribution; thus  $ThCp^*_2Me_2$  reacts with acetone to afford a *tert*-butoxy compound.

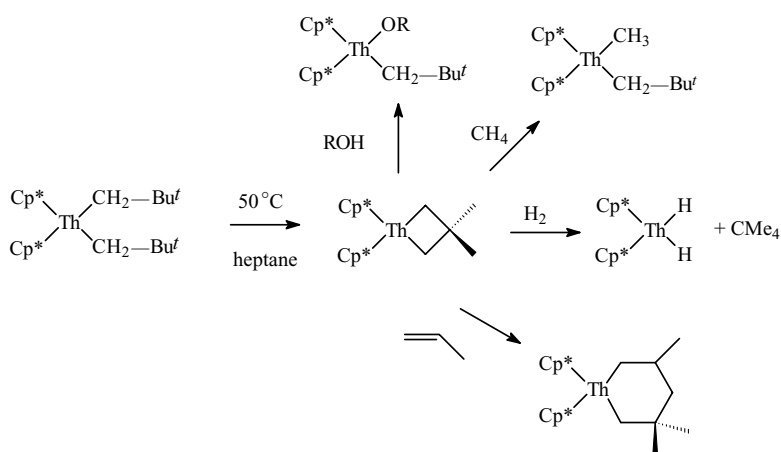
Reactions with  $R'OH$ ,  $R'SH$ , and  $R'_2NH$  afford products such as  $ThCp^*_2(R)(OR')$ ,  $ThCp^*_2(OR')_2$ ,  $ThCp^*_2(SR')_2$ , and  $ThCp^*_2(NR'^2)_2$  ( $R'$ , e.g., Pr;  $R^2$ , e.g., Et).

The compounds  $Cp^*_2Th(CH_2CMe_3)_2$  and  $Cp^*_2Th(CH_2SiMe_3)_2$  undergo most remarkable elimination reactions to form metallacyclic complexes on heating to only 50 °C in toluene solution:



Reactions of  $Cp^*_2Th(CH_2CMe_2-CH_2)$  are shown in Figure 13.7.



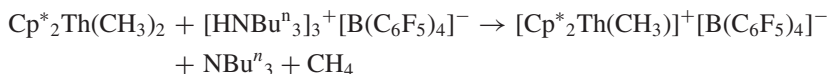


**Figure 13.7**  
Reactions of  $\text{Cp}^*_2\text{Th}(\text{CH}_2\text{CMe}_2\text{-CH}_2)$ .

Some mono( $\text{Cp}^*$ ) complexes are known, reaction of  $\text{MCl}_4$  ( $\text{M} = \text{U}, \text{Th}$ ) with  $\text{MeMgCl} \cdot \text{THF}$  yielding  $[\text{Cp}^*\text{MCl}_3(\text{thf})_2]$ , with structures analogous to the  $[\text{CpLnCl}_2(\text{thf})_3]$  compounds. The halogens can be replaced with the isolation of  $[\text{Cp}^*\text{Th}(\text{CH}_2\text{Ph})_3]$ ; this has a piano-stool structure with  $\text{Th-C}$   $\sigma$ -bonds of 2.578–2.581 Å. There is some interaction between Th and the benzene rings, so this is not a classical  $\eta^1$ -alkyl.

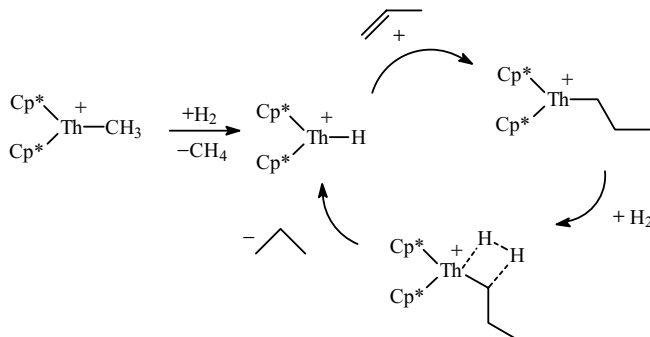
### 13.4.2 Cationic Species and Catalysts

Cationic alkyls have been studied with profit. Thus, in benzene solution,

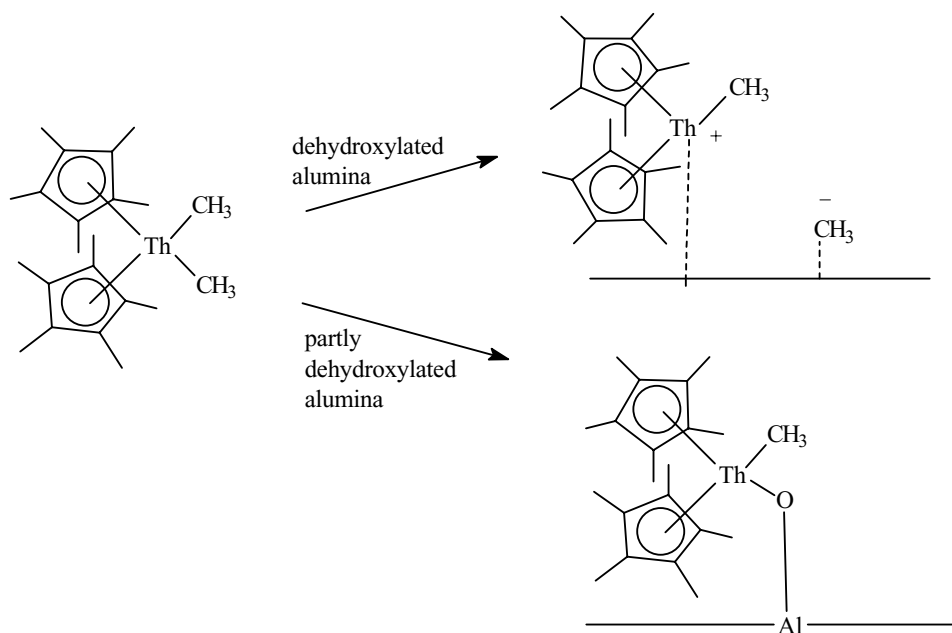


$[\text{Cp}^*_2\text{Th}(\text{CH}_3)]^+ [\text{B}(\text{C}_6\text{F}_5)_4]^-$  in fact has a very weakly bound anion [ $\text{Th-F}$  2.757, 2.675 Å;  $\text{Th-C}$  (ring) 2.754 Å,  $\text{Th-CH}_3$  2.399 Å], so that it is an active catalyst for ethene polymerization and hex-1-ene hydrogenation (Figure 13.8).

If this type of abstraction reaction is carried out in THF,  $[\text{Cp}^*_2\text{Th}(\text{CH}_3)(\text{THF})_2]^+ [\text{BPh}_4]^-$  is formed [ $\text{Th-C}$  (ring) 2.801 Å,  $\text{Th-CH}_3$  2.491 Å].



**Figure 13.8**  
 $[\text{Cp}^*_2\text{ThCH}_3]^+$  as a catalyst for hydrogenation.

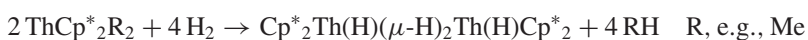


**Figure 13.9**  
Surface bound cationic thorium alkyls.

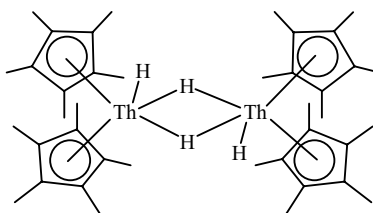
On alumina surfaces cationic alkyls exhibit catalytic activity, due to the formation of coordinatively unsaturated species (Figure 13.9).

### 13.4.3 Hydrides

Striking hydride derivatives are formed, which are efficient catalysts for the homogeneous hydrogenation of hex-1-ene (Figure 13.10):



This remarkable thorium compound is stable to 80 °C. In solution it has rapid hydrogen exchange with dihydrogen gas. Solution  $^1\text{H}$  NMR shows the bridge and terminal hydrogens are equivalent even at  $-90^\circ\text{C}$ . In the solid state,  $\text{Th-H}$  is 2.03 Å (terminal) and 2.29 Å (bridge); a  $\text{Th-Th}$  distance of 4.007 Å indicates minimal metal-metal bonding. In the IR,  $\nu \text{Th-H}$  (terminal) vibrations occur at 1404 and 1336  $\text{cm}^{-1}$ ; bridging vibrations occur at 1215, 1114, 844, and 650  $\text{cm}^{-1}$ .  $\text{Cp}^*_2\text{U}(\text{H})(\mu\text{-H})_2\text{U}(\text{H})\text{Cp}^*_2$  can be made too but tends to



**Figure 13.10**  
Structure of  $[\text{Cp}^*_2\text{Th}(\text{H})(\mu\text{-H})_2\text{Th}(\text{H})\text{Cp}^*_2]$ .

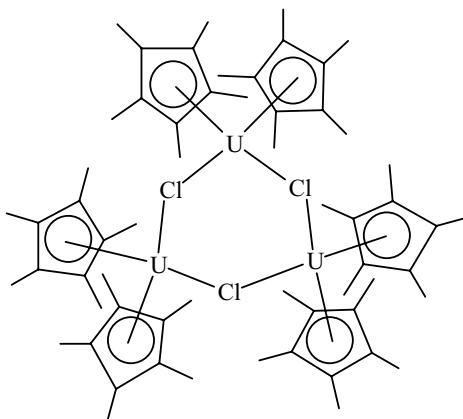
decompose to a  $\text{U}^{\text{III}}$  hydride  $\text{Cp}^*_2\text{U}(\text{H})$ , which can be isolated and stabilized as a DMPE complex  $[\text{Cp}^*_2\text{U}(\text{H})\{\text{Me}_2\text{P}(\text{CH}_2)_2\text{PMe}_2\}]$ .

Attempted conversion of  $\text{UCp}^*_2\text{RCl}$  into a hydride gives the uranium (III) compound  $\text{UCp}^*_2\text{Cl}$  (Section 13.4.4).

The hydrides are reactive and readily react with halogenocarbons, alcohols, and ketones; alkenes afford alkyls.

### 13.4.4 Oxidation State (III)

Hydrogen reduction of  $[\text{UCp}^*_2\text{ClR}]$  gives trimeric  $\text{UCp}^*_2\text{Cl}$  (Figure 13.11).



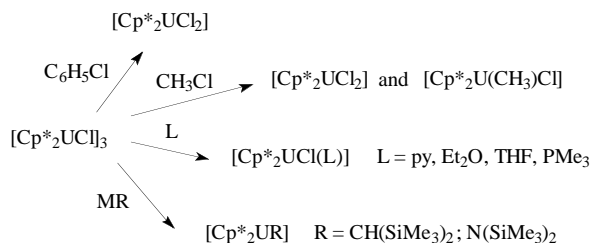
**Figure 13.11**

The structure of trimeric  $[\text{Cp}^*_2\text{UCl}]_3$ .

In the similar reaction with  $\text{R} = \text{methyl}$ , the organic product is  $\text{CH}_4$ . If the reaction is carried out with the analogous thorium starting material,  $\text{ThCp}^*_2\text{Cl}(\text{R})$  forms the thorium(IV) compound  $[\text{Cp}^*_2\text{Th}(\mu\text{-H})\text{Cl}]_2$ .

The uranium compound has a cyclic trimeric structure. Each uranium is individually in pseudotetrahedral coordination. It undergoes various reactions (Figure 13.12).

These may be classed as straightforward substitutions using a bulky anionic ligand; adduct formation with Lewis bases retaining pseudotetrahedral coordination; and redox. The photoelectron spectrum of the alkyl  $[\text{UCp}^*_2(\text{CH}_2\text{SiMe}_3)]$  indicates a  $5f^3$  ground state but also that the  $5f^26d^1$  state is only slightly higher in energy.

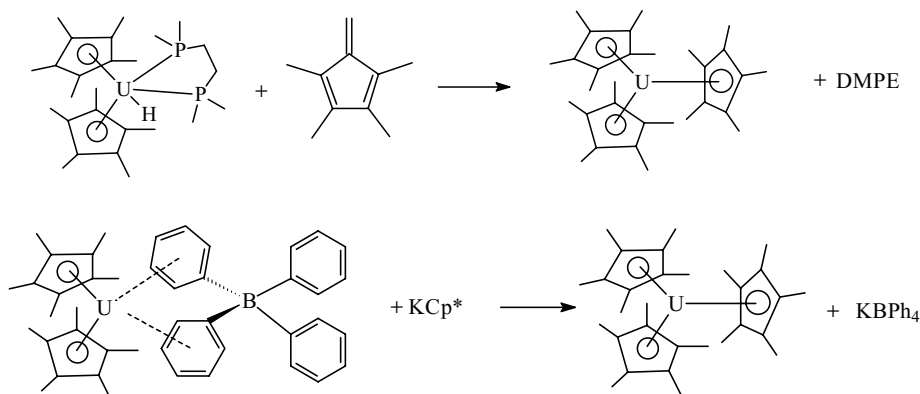


**Figure 13.12**

Reactions of  $[\text{Cp}^*_2\text{UCl}]_3$ .

### 13.5 Tris(pentamethylcyclopentadienyl) Systems

For many years it was believed that  $[\text{LnCp}^*_3]$  systems could not be made. After the successful isolation of  $[\text{SmCp}^*_3]$  and similar compounds (Section 6.3.2), attention turned to the possibility of isolating the uranium analogue. The hydride  $\text{Cp}^*_2\text{UH}(\text{dmpe})$  proved to be a useful starting point, reacting with either tetramethylfulvalene or  $\text{PbCp}^*_2$  to form  $[\text{UCp}^*_3]$ , but routes analogous to those used for lanthanides have also worked (Figure 13.13).



**Figure 13.13**  
Synthesis of  $[\text{UCp}^*_3]$ .

With the isolation of  $[\text{UCp}^*_3]$  accomplished, the next target was what promised to be even harder, the synthesis of the uranium(IV) species  $[\text{UCp}^*_3\text{Cl}]$  and related compounds.  $[\text{UCp}^*_3]$  underwent oxidation with  $\text{HgF}_2$ , forming  $[\text{UCp}^*_3\text{F}]$ , and reaction with a stoichiometric amount of  $\text{PhCl}$ , forming  $[\text{UCp}^*_3\text{Cl}]$ ; reaction of  $[\text{UCp}^*_3]$  with 2 molecules of  $\text{PhCl}$  afforded  $[\text{UCp}^*_2\text{Cl}_2]$ .

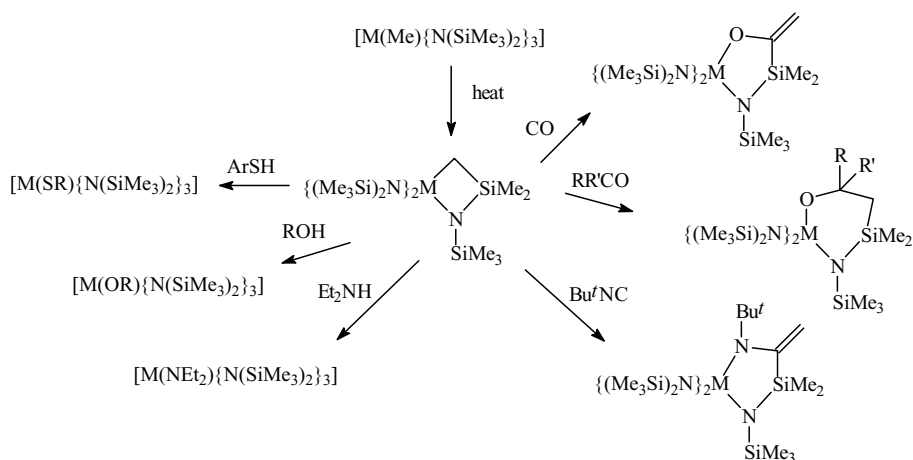
The structure of  $[\text{UCp}^*_3]$  has trigonal planar coordination of U; similarly in  $[\text{UCp}^*_3\text{Cl}]$ ; the three ring centroids are coplanar with U, and with a very long U–Cl bond at 2.90 Å – compare 2.637 Å in  $[\text{U}(\text{C}_5\text{Me}_4\text{H})_3\text{Cl}]$ .

### 13.6 Other Metallacycles

$\text{Cp}^*_2\text{Th}(\text{CH}_2\text{CMe}_2\text{-CH}_2)$  has already been mentioned. Another kind of metallacycle has been synthesized from the alkyls  $[\text{M}(\text{CH}_3)\{\text{N}(\text{SiMe}_3)_2\}_3]$  ( $\text{M} = \text{Th}, \text{U}$ , see Section 11.8.1). They undergo thermolysis in benzene solution to afford  $[\{(\text{Me}_3\text{Si})_2\text{N}\}_2\text{M}\{\text{N}(\text{SiMe}_3)(\text{SiMe}_2)\}]$ . These in turn have a rich chemistry (Figure 13.14), undergoing insertion reactions with CO, carbonyl compounds, nitriles, and isocyanides. In the reactions involving compounds with acidic hydrocarbons, such as tertiary alcohols, phenols, and thiols, the metallacyclic ring is broken to re-form the amide ligand.

### 13.7 Cyclooctatetraene Dianion Compounds

These are regarded as derivatives of the  $\text{C}_8\text{H}_8^{2-}$  ligand; substituted rings also occur. Uranocene,  $\text{U}(\eta^8\text{-C}_8\text{H}_8)_2$ , was reported in 1968 (A. Streitwieser, Jr., and V. Mueller-Westerhoff,

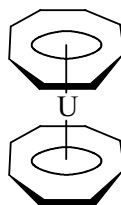
**Figure 13.14**

Synthesis and reactions of the metallacycles  $\{(\text{Me}_3\text{Si})_2\text{N}\}_2\text{M}\{\text{N}(\text{SiMe}_3)(\text{SiMe}_2)\}$ .

*J. Am. Chem. Soc.*, 1968, **90**, 7364) and was a seminal compound in the development of the organometallic chemistry of the actinides. It was made by a general route:



The Pu analogue was made from  $(\text{pyH})_2\text{PuCl}_6$ , since plutonium does not form a tetrachloride. All five compounds are isomorphous and believed to have similar sandwich structures, with the two (planar) 8-membered rings in the eclipsed configuration (Figure 13.15).

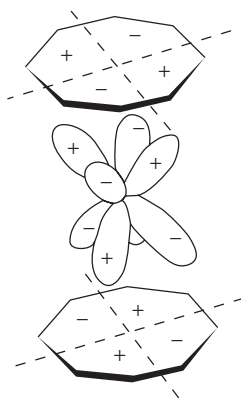
**Figure 13.15**

Structure of uranocene,  $[\text{U}(\text{C}_8\text{H}_8)_2]$ .

Uranocene forms green crystals that are pyrophoric in air, but it is otherwise rather unreactive, not readily hydrolysed by water or even acetic acid. It is stable to vacuum sublimation at  $200^\circ\text{C}$ . The other  $\text{M}(\eta^8\text{-C}_8\text{H}_8)_2$  are more reactive and easily hydrolysed. A mean bond-dissociation energy of  $347 \text{ kJ mol}^{-1}$  has been measured for  $\text{U}(\eta^8\text{-C}_8\text{H}_8)_2$ ; it is substantially greater than the value of  $247 \text{ kJ mol}^{-1}$  for  $\text{U}(\text{C}_5\text{H}_5)_4$ . Of substituted uranocenes, two stand out.  $[\text{U}(1,3,5,7\text{-Me}_4\text{C}_8\text{H}_4)_2]$  exists in the crystal as a mixture of the 'eclipsed' and 'staggered' rotamers, whilst  $[\text{U}(1,3,5,7\text{-Ph}_4\text{C}_8\text{H}_4)_2]$  (present in the crystal with phenyls staggered in the two different rings) sublimates at  $400^\circ\text{C}$ ,  $10^{-5} \text{ mmHg}$ , and is totally air stable, doubtless owing to the phenyl groups hindering access of oxygen molecules to the uranium atom.

Some sandwich compounds  $[\text{K}(\text{solvent})][\text{M}(\eta^8\text{-RC}_8\text{H}_7)_2]$  ( $\text{M} = \text{U, Np, Pu, Am}$ ;  $\text{R}$ , e.g.,  $\text{H, Me}$ ) may also be made in the +3 state by analogous reactions starting from:



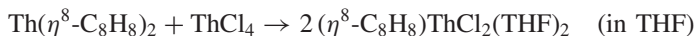
**Figure 13.16**

Possible f-orbital involvement in the bonding in uranocene.

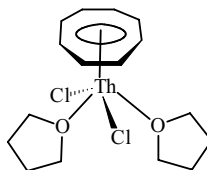
Bonding in uranocene has been the subject of controversy for some 30 years. It was early on pointed out that orbital symmetry interactions, involving f orbitals, could be drawn analogous to those in ferrocene (Figure 13.16).

More sophisticated MO calculations, especially including relativistic corrections, suggest that whilst uranium 6d orbitals interact with the ligand orbitals, the 5f orbitals are relatively unperturbed. Photoelectron spectra do suggest that 5f interaction increases as more alkyl groups are introduced into the cyclooctatetraene rings.

Half-sandwich compounds have been made, in the case of thorium by redistribution:

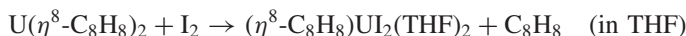


This compound has a piano-stool-type structure (Figure 13.17).

**Figure 13.17**

Structure of the 'half-sandwich'  $[\text{Th}(\text{C}_8\text{H}_8)\text{Cl}_2(\text{THF})_2]$ .

Uranium analogues can be made, not always by identical routes:



## 13.8 Arene Complexes

The reaction between  $\text{UCl}_4$ , Al, and  $\text{AlCl}_3$  in refluxing benzene affords  $[(\eta^6\text{-C}_6\text{H}_6)\text{U}\{(\mu\text{-Cl})_2\text{AlCl}_4\}_3]$ . (Figure 13.18).

Certain other compounds of this type are known in the (+3) state, such as  $[(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)\text{U}(\text{BH}_4)_3]$ ; also dimeric  $[(\text{C}_6\text{Me}_6)_2\text{U}_2\text{Cl}_7]^+ (\text{AlCl}_4)^-$ , which is  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Cl}_2\text{U}(\mu\text{-Cl})_3\text{UCl}_2(\eta^6\text{-C}_6\text{Me}_6)]^+ (\text{AlCl}_4)^-$ . These are considerably more reactive than uranocene.

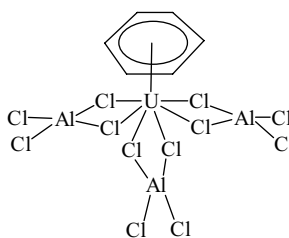


Figure 13.18

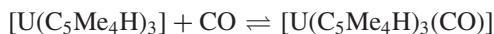
However, in contrast to the lanthanides, no arene complexes in a formal zero oxidation state have been isolated.

### 13.9 Carbonyls

The early transition metals are conspicuous in forming binary carbonyls like  $M(CO)_6$  ( $M = Cr, Mo, W$ );  $M'(CO)_5$  ( $M' = Fe, Ru, Os$ ); and  $Ni(CO)_4$ , which have considerable thermal stability.

Co-condensation of uranium atoms with CO in an argon matrix at 4 K followed by annealing gives carbonyls  $U(CO)_n$  detectable by IR, but which decompose above 20 K (as do those of the lanthanides). A complex identified as  $U(CO)_6$  has  $\nu_{CO}$  at  $1961\text{ cm}^{-1}$ , very similar to that in  $W(CO)_6$  ( $1987\text{ cm}^{-1}$ ), a significant decrease from the value of  $2145\text{ cm}^{-1}$  in CO itself, indicating a substantial amount of  $\pi$ -donation by uranium.

However, unlike the lanthanides, some stable carbonyl complexes in normal oxidation states have been identified for uranium. No adduct has been identified for  $[UCp_3]$  but  $U\{C_5H_4(SiMe_3)\}_3$  reversibly combines with CO in both the solid state and hexane solution, the latter with a colour change from deep green to burgundy, and the appearance of  $\nu_{CO}$  at  $1976\text{ cm}^{-1}$  in the IR spectrum.  $[U\{C_5H_3(SiMe_3)_2\}_3]$  forms a similarly detectable but non-isolable CO adduct; however, an adduct  $[U(C_5Me_4H)_3(CO)]$  has been isolated in the solid state, starting from  $[U(C_5Me_4H)_3]$ :



It has a linear U–CO linkage, with U–C  $2.383\text{ \AA}$ , and C–O slightly lengthened from  $1.128\text{ \AA}$  in free CO to  $1.142\text{ \AA}$ .  $\nu_{CO}$  occurs at  $1880\text{ cm}^{-1}$  in  $[U(C_5Me_4H)_3(CO)]$ , shifted to  $1840\text{ cm}^{-1}$  in  $[U(C_5Me_4H)_3(^{13}CO)]$  and  $1793\text{ cm}^{-1}$  in  $[U(C_5Me_4H)_3(C^{18}O)]$ .

**Question 13.1** Suggest why, at the time of the Manhattan project in the 1940s, Gilman attempted the synthesis of simple uranium alkyls and aryls as vehicles for isotope separation.

**Answer 13.1** At that time, few d-block alkyls and aryls were known. Gilman would have reasoned that by analogy with compounds of the Group IV elements like carbon and silicon, uranium(IV) alkyls and aryls might have simple molecular structures and thus be volatile.

**Question 13.2** Why are simple actinide alkyls rare in view of the number of lanthanide species like  $[M\{CH(SiMe_3)_2\}_3]$ ,  $[LnPh_3(thf)_3]$ , and  $[LnMe_6]^{3-}$  (see Chapter 5)?

**Answer 13.2** Good question! There are several possible reasons. One is that most studies have involved uranium, where there may be redox problems (note that  $CH_3Li$  reduces  $Eu^{3+}$ , too). Another is that the later actinides, which might be expected on size grounds to form

compounds in the +3 state similar to those of the lanthanides, are very inaccessible owing to radioactivity and non-availability of starting materials.

**Question 13.3** Predict the products of the reaction of  $[\text{Cp}_3\text{UCl}]$  with (a)  $\text{LiNEt}_2$ , (b)  $\text{LiSiPh}_3$ , (c)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Li}$ , (d)  $\text{C}_6\text{H}_5\text{CH}_2\text{MgBr}$ . Would you expect  $[\text{Cp}_3\text{U}(\text{SCN})]$  to have U–S or a U–N bond? Why?

**Answer 13.3** (a)  $[\text{Cp}_3\text{U}(\text{NEt}_2)]$ ; (b)  $[\text{Cp}_3\text{U}(\text{SiPh}_3)]$ ; (c)  $[\text{Cp}_3\text{U}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3)]$ ; (d)  $[\text{Cp}_3\text{U}(\text{CH}_2\text{C}_6\text{H}_5)]$ .  $[\text{Cp}_3\text{U}(\text{SCN})]$  is N-bonded, owing to the preference of uranium for the ‘hard’ donor N.

**Question 13.4** Attempts to make the *tert*-butyl compound  $\text{ThCp}^*_2(\text{CMe}_3)_2$  by the reaction of  $\text{ThCp}^*_2\text{Cl}_2$  with *tert*-butyllithium were unsuccessful, the hydride  $\text{ThCp}^*_2\text{H}_2$   $\{\text{Cp}^*_2\text{Th}(\text{H})(\mu\text{-H})_2\text{Th}(\text{H})\text{Cp}^*_2\}$  being obtained. Suggest why.

**Answer 13.4** The most likely answer is a steric one; attaching two bulky *tert*-butyl groups to the  $\text{Cp}^*_2\text{Th}$  unit would result in a very congested environment.

**Question 13.5** Read Section 13.4.1. Suggest a reason for the reaction of  $\text{ThCp}^*_2(\text{CH}_2\text{CMe}_3)_2$  in forming a cyclic compound, also a reason for the reactivity of the metalla-cycles.

**Answer 13.5** The agostic  $\text{Th}\cdots\text{H}-\text{C}$  interactions in the structure of  $\text{ThCp}^*_2(\text{CH}_2\text{CMe}_3)_2$  referred to earlier hint that these molecules may be congested. The cyclic compounds contain a 4-membered ring; presumably the reactions relieve the strain.

**Question 13.6** How would you confirm IR assignments for the bridged hydride  $[\text{Cp}^*_2\text{Th}(\text{H})(\mu\text{-H})_2\text{Th}(\text{H})\text{Cp}^*_2]$ ?

**Answer 13.6** Since the hydride groups are labile, isolating the deuterated compound by exchange under a  $\text{D}_2$  atmosphere in solution should be straightforward.

**Question 13.7** Suggest why the uranium compound  $[\text{Cp}^*_2\text{U}(\text{H})(\mu\text{-H})_2\text{U}(\text{H})\text{Cp}^*_2]$  is less stable than the thorium analogue.

**Answer 13.7** The +3 oxidation state is more accessible for uranium and so facilitates a decomposition pathway.

**Question 13.8** Of the adducts  $[\text{UCp}^*_2(\text{CH}_2\text{SiMe}_3)\text{L}]$  ( $\text{L} = \text{PMe}_3$ , py,  $\text{Et}_2\text{O}$ , THF), the Lewis base is most easily removed from the  $\text{PMe}_3$  adduct. Suggest why.

**Answer 13.8** Tertiary phosphines are ‘soft’ bases and actinides are ‘hard’ acids. This is likely to be the weakest linkage thermodynamically.

**Question 13.9** The U–C and Th–C bond lengths are 2.647 and 2.701 Å, respectively, in  $\text{M}(\eta^8\text{-C}_8\text{H}_8)_2$  ( $\text{M} = \text{U}, \text{Th}$ ). In  $[\text{K}(\text{diglyme})][\text{U}(\eta^8\text{-MeC}_8\text{H}_7)_2]$  the U–C bond length averages 2.719 Å. Explain these values.

**Answer 13.9** The ionic radius of  $\text{Th}^{4+}$  is greater than that of  $\text{U}^{4+}$ , whilst the radius of  $\text{U}^{3+}$  is greater than that of  $\text{U}^{4+}$ .

**Question 13.10** Comment upon the C–O bond length and IR data for  $[\text{U}(\text{C}_5\text{Me}_4\text{H})_3(\text{CO})]$  (hint, remember  $E = h\nu$ ). The C–O distance is slightly lengthened from 1.128 Å in free CO to 1.142 Å.  $\nu_{\text{CO}}$  occurs at  $1880\text{ cm}^{-1}$  in  $[\text{U}(\text{C}_5\text{Me}_4\text{H})_3(\text{CO})]$ , shifted to  $1840\text{ cm}^{-1}$  in



$[\text{U}(\text{C}_5\text{Me}_4\text{H})_3(^{13}\text{CO})]$  and  $1793\text{ cm}^{-1}$  in  $[\text{U}(\text{C}_5\text{Me}_4\text{H})_3(\text{C}^{18}\text{O})]$ . It occurs at  $2145\text{ cm}^{-1}$  in CO itself.

**Answer 13.10** The C–O bond lengthens upon coordination, showing that it is getting weaker. This can be explained in terms of uranium (5f) to CO ( $2\pi$ ) back-bonding, with electrons introduced into ligand  $\pi^*$  antibonding orbitals (thus weakening the bond). The CO stretching frequency moves to lower frequency, also indicating bond weakening. This frequency also decreases on introducing C or O atoms of higher mass, confirming that vibrations of these atoms were indeed involved.

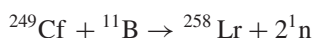
# 14 Synthesis of the Transactinides and their Chemistry

By the end of this chapter you should be able to:

- recognize that the transactinide elements have very short half-lives;
- know that studying their chemistry presents serious practical difficulties;
- appreciate ways in which these elements may be synthesized and their chemistry studied;
- have some knowledge of the chemistry of elements 104–108 and relate them to their neighbours in the Periodic Table;
- appreciate how the principles of the Periodic system may be used to predict the properties of other elements yet to be made and studied.

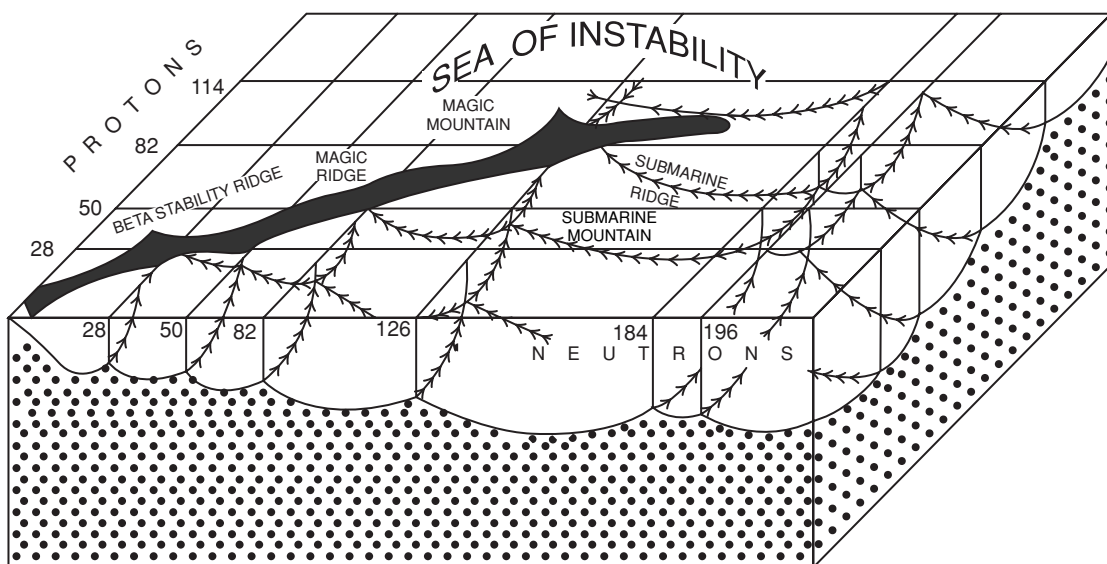
## 14.1 Introduction

As noted in Section 9.2, the heavier actinides were made an ‘atom at a time’. The last one, lawrencium, was synthesized in 1961 by bombarding a target of californium isotopes (masses 249–252) with  $^{10}\text{B}$  and  $^{11}\text{B}$  nuclei. The isotope  $^{258}\text{Lr}$  has a half-life of 3.8 s.



Chemical studies were not possible until 1970 with the synthesis of longer-lived  $^{256}\text{Lr}$  ( $t_{1/2} = 26$  s). The even more stable neutron-rich  $^{262}\text{Lr}$  with a half-life of 3.6 hours is now known. At the time, though, there seemed few prospects of extending the Periodic Table into another series and in any case it was also not clear what chemical properties were expected for these elements, nor how they might be studied. Experience with the actinides had shown that half-lives for  $\alpha$ -decay of each element were steadily growing shorter as the atomic number increased, whilst the drop in half-lives for spontaneous fission was even more dramatic. Extrapolation to elements with atomic numbers around 107–108 indicated that half-lives would be so short ( $t_{1/2} = 10^{-3}$  s) that it would be impossible to isolate further elements.

Theoreticians thought that stable heavier elements might be in prospect. The stability of a nucleus (based on a model of nuclear stability analogous to that of the Rutherford–Bohr model of electronic structure) is determined by the inter-nucleon forces (nucleons are protons and neutrons), an attractive force between all nucleons and a Coulombic repulsion force between protons, the latter becoming proportionately more important as the number of protons increases. Extra stability is associated with filled shells of nucleons, ‘magic numbers’; for neutrons they are 2, 8, 20, 28, 50, 82, 126, 184, and 196; and for protons they are 2, 8, 20, 28, 50, 82, 114, and 164.



**Figure 14.1**

Known and predicted regions of nuclear stability (reproduced with permission from G.T. Seaborg, *J. Chem. Educ.*, 1969, **46**, 631).

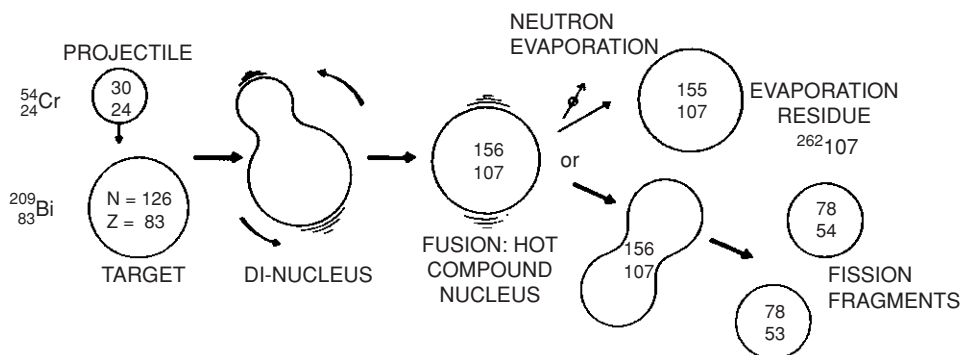
Nuclei with closed shells of nucleons are stabilized, particularly against spontaneous fission. Nuclei where the numbers of protons and neutrons are both magic numbers ('double-magic' nuclei) are particularly stable, such as  $^4\text{He}$ ,  $^{16}\text{O}$ ,  $^{40}\text{Ca}$ , and  $^{208}\text{Pb}$ . After  $^{208}\text{Pb}$ , the next 'double-magic' nucleus would be  $^{298}114$ . The stability of nuclei can be represented on 3-D maps (Figure 14.1), with peaks corresponding to the stablest 'magic number' nuclei. Originally element 114 was represented by an 'island of stability' but new calculations suggest relatively stable nuclei may extend towards it. In the past thirty years, elements 104–116 and 118 have all been reported and some chemistry of elements 104–108 investigated. These investigations represent one of the greatest scientific achievements.

## 14.2 Finding New Elements

Unsuccessful attempts were made to find elements with  $Z \sim 110$ – $114$  in case they were stable. Searches for element 110 ('eka-platinum') in platinum metal ores led to negative results, corresponding to a limit of  $10^{-11}$  g per g of stable element. Similar inconclusive results were obtained looking for element 114 ('eka-lead') in lead ores. Scientists therefore attempted to synthesize these new elements, using essentially the same methods used for the later actinides.

## 14.3 Synthesis of the Transactinides

Discovery of these elements has largely resulted from the researches of three groups: from Russian scientists at the Joint Institute for Nuclear Research (JINR), Dubna; German workers at the Gesellschaft für Schwerionenforschung (GSI), Darmstadt; and Americans,

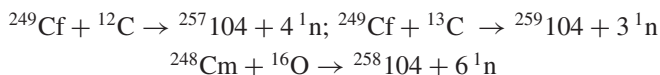
**Figure 14.2**

Synthesis of element 107 by nuclear fusion (reproduced with permission from G. Herrmann, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1421).

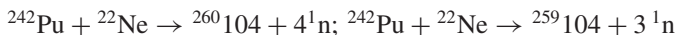
principally at the Lawrence Berkeley National Laboratory, Berkeley, California; recent contributions have come from Japanese workers at the RIKEN Linear Accelerator Facility. The approach used is to bombard a target nucleus (generally an actinide) with the positively charged nuclei of other elements, using a particle accelerator (cyclotron or linear accelerator) to supply the high energy needed to overcome the repulsion between the positively charged target nucleus and positive projectile nucleus, as already discussed in Section 9.2. In this method the atoms are produced one at a time, obviating 'normal' chemical experiments on bulk samples. The chance of a collision producing a combined nucleus is at best about one in a billion collisions.

Moreover, since the new atomic nucleus produced is in an excited nuclear state, it has an excess of energy to get rid of, whether by emission of neutrons and  $\gamma$ -rays, or by fission (Figure 14.2) (If the energy of the bombarding particles is too low, they do not possess enough energy to overcome the Coulombic repulsion between them.)

For elements 104 and 105, competing claims of first discovery have been made by the American and Russian teams. In 1969 workers from Berkeley reported the synthesis of  $^{257-259}_{104}$ :



Almost simultaneously an alternative route was reported by the Dubna workers:

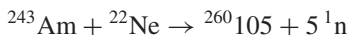


Since different isotopes of the transactinides have frequently been reported from different synthetic routes, it has been very difficult to decide who 'discovered' a new element.

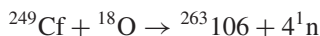
Element 105 was reported by the Berkeley group in 1970 and the Dubna group in 1971. The Berkeley team used



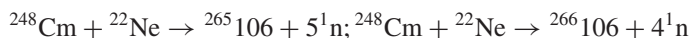
whilst the Dubna group employed



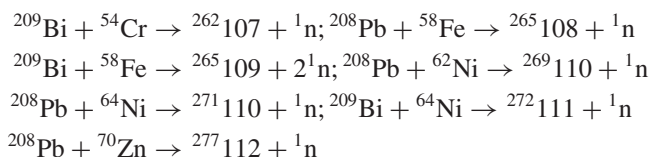
The original (1974) synthesis of element 106 by the Berkeley group was repeated there by a different team in 1993:



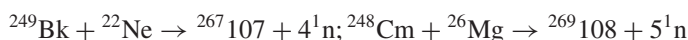
whilst heavier isotopes of mass 265 and 266 with half-lives of 7 s. and 21 s, respectively, suitable for chemical studies, are now known.



Elements 107–112 were initially synthesized by the Darmstadt group, though subsequently other isotopes have been made by the other groups or detected in the decay chains of heavier nuclei. Their syntheses used rather heavier projectile atoms and concomitantly lighter targets; this is sometimes called a ‘cold-fusion’ approach (not to be confused with the notorious room-temperature fusion reactions reported in 1989 as a route to ‘limitless energy’). This method uses projectile particles with the minimum kinetic energy to just result in fusion so that the product nucleus has little excessive energy to get rid of, so that not only is the likelihood of fission minimized, but very few neutrons ‘evaporate’ from the ‘hot’ nucleus, so that the mass number of the resulting product is as high as possible. Another significant point is that the Pb and Bi targets have magic- or near-magic-number structures, as do the nickel projectile nuclei used in the syntheses of elements 110 and 111, so that a large part of the projectile energy is consumed in breaking into the filled shell and this also reduces the possibility of the new nucleus undergoing fission.

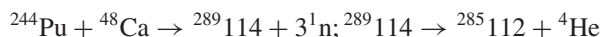


A different approach to element 107 has led to an isotope with a half-life of 14 s, used in chemical studies; similarly, synthesis of  $^{269}108$  with a half-life of around 11 s has permitted the first chemical investigations of element 108.



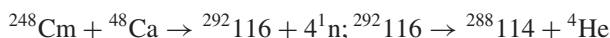
In 1999–2000, syntheses of elements 114, 116, and 118 were first reported, but the results for experiment 118 have proved to be irreproducible, so it cannot yet be claimed to have been made.

Bombardment of  $^{244}\text{Pu}$  with neutron-rich  $^{48}\text{Ca}$  for several weeks led to reports of one atom of element 114. The atom had a lifetime of about 30 s before decaying to form an atom of element 112:



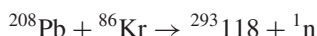
Particularly long-lived atoms detected in the decay chain were identified as isotopes of elements 112 and 108 with respective lifetimes of around 15 minutes. Other isotopes  $^{287}114$  and  $^{288}114$  have also been reported.

A similar route, bombardment of  $^{248}\text{Cm}$  with  $^{48}\text{Ca}$ , was used to make element 116 (Uuh); it alpha-decayed after 47 ms to a known isotope of element 114:

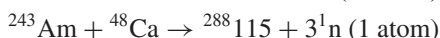
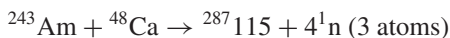


Isotopes  $^{290}116$  and  $^{291}116$  have also been reported.

An alternative route was followed by workers at LBNL in California, who used a ‘cold fusion’ approach with a heavier projectile nucleus (krypton) and a lighter target (lead); bombardment over an eleven-day period afforded three atoms having a lifetime of less than a millisecond, believed to be element 118, though these claims must be regarded as unsubstantiated.



Most recently, in February 2004, experiments were reported giving serious evidence for elements 113 and 115, again synthesized using  $^{48}\text{Ca}$  as the projectile:

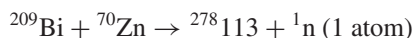


These atoms all decayed (with lifetimes in the range 19–280 milliseconds) by  $\alpha$ -decay to afford what are believed to be atoms of element 113:



These atoms of element 113 have longer lifetimes, one in excess of a second.

An alternative route for synthesis of an atom of element 113 was reported by a team of Japanese (largely) and Chinese workers in October 2004:



This decayed with a lifetime of 344 ms to an isotope of element 111.



## 14.4 Naming the Transactinides

The two groups who claim to have synthesized elements 104 and 105 gave them both a name. The International Union of Pure and Applied Chemistry therefore suggested a system of surrogate names for these elements until definite identification could be credited; this assigned each element a name based on its atomic number, using the ‘code’ 0 = nil, 1 = un, 2 = bi, 3 = tri, 4 = quad, 5 = pent, 6 = hex, 7 = sept, 8 = oct, and 9 = enn. Thus element 104 is unnilquadium.

In 1997, the International Union of Pure and Applied Chemistry decided names for elements 104–109, which have generally met with acceptance; they have recently decided names for 110 (2003) and for 111 (2004).

No decisions have yet been made about the heavier elements.

**Table 14.1**

Atomic number	Name	Symbol
104	Rutherfordium	Rf
105	Dubnium	Db
106	Seaborgium	Sg
107	Bohrium	Bh
108	Hassium	Hs
109	Meitnerium	Mt
110	Darmstadtium	Ds
111	Roentgenium	Rg

## 14.5 Predicting Electronic Arrangements

The 5f orbitals are gradually filled as the actinide series is crossed and there is general agreement that the 6d orbitals will be filled next, followed by 7p orbitals. Table 14.2 lists predicted electron configurations.

**Table 14.2** Election configurations of elements 104–121<sup>a</sup>

Element	6d	7s	7p <sub>1/2</sub>	7p <sub>3/2</sub>	8s	7d (or 8p <sub>1/2</sub> )
104	2	2				
105	3	2				
106	4	2				
107	5	2				
108	6	2				
109	7	2				
110	8	2				
111	9	2				
112	10	2				
113	10	2	1			
114	10	2	2			
115	10	2	2	1		
116	10	2	2	2		
117	10	2	2	3		
118	10	2	2	4		
119	10	2	2	4	1	
120	10	2	2	4	2	
121	10	2	2	4	2	1

<sup>a</sup> Electron configurations are given outside the core [Rn] 5f<sup>14</sup>.

## 14.6 Identifying the Elements

Classical chemical routes are impractical with ultrasmall quantities of very radioactive, short-lived atoms. Even the most stable transactinides have such short half-lives (Table 14.3) that they had to be rapidly removed from the accelerator target for chemical study. This is achieved by the recoil of the new atom from the target and its transport by an aerosol in a current of helium to a collection site. Figure 14.3 shows the system used to study the chlorination of elements 104 and 105, using an MoO<sub>3</sub> aerosol to transport the atoms prior to halogenation. The volatile halides formed are transported by the helium along the latter part of the tube, which acts as an isothermal gas chromatography column; on leaving the quartz tube they are attached to new aerosols and detected either with a rotating wheel system or on a moving computer tape.

The millisecond half-lives of the first isotopes of elements 107–112 meant that there was no chance of carrying out chemical separations, so the Darmstadt group have used a ‘velocity filter’ which relies on electric and magnetic fields to separate the excess of fast-moving ‘projectile’ nuclei from slow-moving products recoiling from the target so that the reaction products can be detected (Figure 14.4). The beams of particles are focussed with magnetic lenses and then separated by electric and magnetic fields before colliding with solid-state detectors.

**Table 14.3** Half-lives and decay modes for the isotopes of elements 104–116 and 118

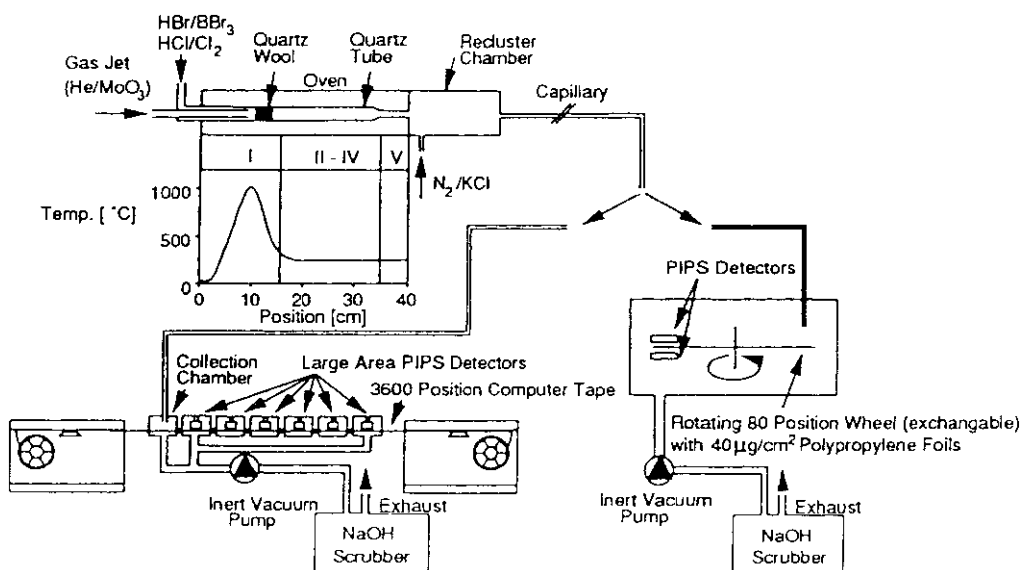
Element	Half-life	Decay mode
104		
253	0.05 ms	SF
254	0.5 ms	SF
255	1.4 s	SF, $\alpha$
256	7 ms	$\alpha$ , SF
257	4.8 s	$\alpha$ , SF
258	13 ms	SF, $\alpha$ ?
259	3.0 s	$\alpha$ , SF
260	20 ms	SF
261	78 s	$\alpha$ , SF
262	47 ms	SF?
263	10 m	$\alpha$ , SF
105		
255	1.6 s	$\alpha$ , SF
256	2.6 s	EC, $\alpha$
257	1.3 s	$\alpha$ , SF
258	20 s	EC, $\alpha$
259		$\alpha$
260	1.5 s	$\alpha$ , SF
261	1.8 s	$\alpha$ , SF
262	34 s	$\alpha$ , SF
263	27 s	SF, $\alpha$
265	7.4 s	$\alpha$
266	21 s	$\alpha$
106		
258	2.9 ms	SF
259	0.9 s	$\alpha$ , SF
260	3.6 ms	$\alpha$ , SF
261	0.23 s	$\alpha$ , SF?
263	0.8 s	$\alpha$ , SF
265	16 s	$\alpha$
266	21 s	$\alpha$
107		
260		$\alpha$
261	12 ms	$\alpha$ , SF?
262	8 ms/0.1 s	$\alpha$
264	0.44 s	$\alpha$
267	17 s	$\alpha$
108		
263	<0.1 s	$\alpha$
264	0.08 ms	$\alpha$ , SF
265	1.8 ms	$\alpha$
267	33 ms	$\alpha$
269	11 s	$\alpha$
270	3.6 s	$\alpha$
273	1.2 s	$\alpha$
277	11.4 m	$\alpha$
109		
266	3.4 ms	$\alpha$
268	70 ms	$\alpha$

*Continued*



**Table 14.3** *Continued*

Element	Half-life	Decay mode
110		
267	4 $\mu$ s	$\alpha$
269	0.17 ms	$\alpha$
271	1.1 ms	$\alpha$
273	0.1 s/0.1 ms	$\alpha$
277		
280	7.4 s	SF
281	1.1 m	$\alpha$
111		
272	1.5 ms	$\alpha$
112		
277	242 $\mu$ s	$\alpha$
281		
283	3 m	SF
284	9.7 s	$\alpha$
285	10.7 m	$\alpha$
113		
283	$\sim$ 1 s	$\alpha$
284	$\sim$ 0.4 s	$\alpha$
114		
285	<1 ms	$\alpha$
287	5 s	$\alpha$
288	1.9 s	$\alpha$
289	$\sim$ 21 s	$\alpha$
115		
287	$\sim$ 46 ms	$\alpha$
288	20–200 ms	$\alpha$
116		
289	47 ms	$\alpha$
118		
293		$\alpha$



**Figure 14.3**

Apparatus for the study of the volatile halides of elements 104 and 105 (reproduced with permission from J.V. Kratz, *J. Alloys Compd.*, 1994, **213–214**, 22).

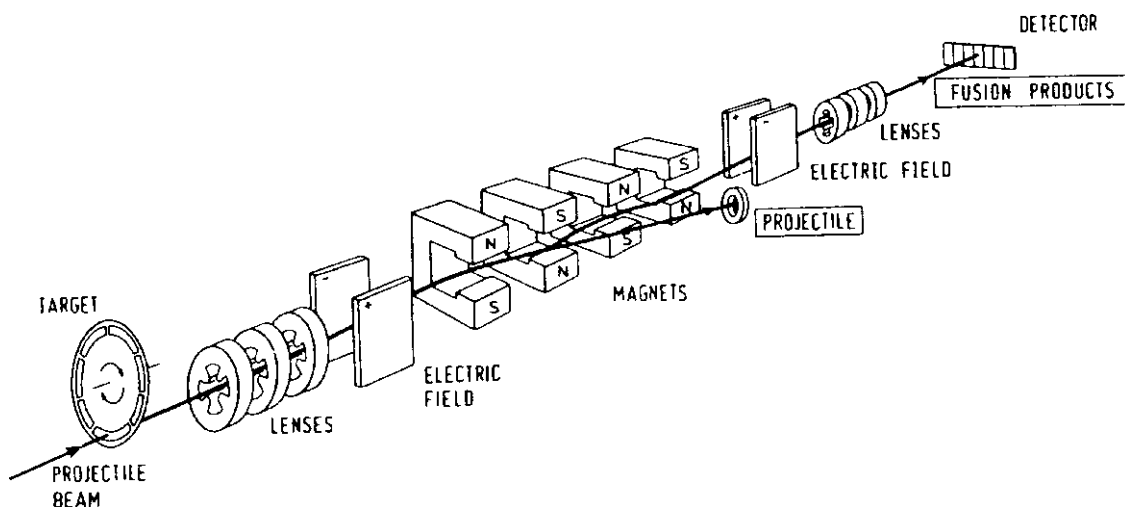
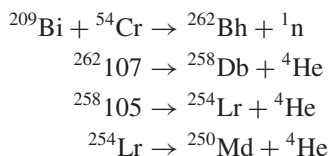


Figure 14.4

Velocity filter SHIP to separate transactinide fusion products from the projectile beam (reproduced with permission from G. Herrmann, *Angew. Chem., Int. Ed. Engl.*, 1988, 27, 1422).

Detection of these elements relies on studying their radioactive decay, which is usually either  $\alpha$ -emission or spontaneous fission. A time-correlation process is used; in this, a solid-state detector monitors both the time and position of arrival of fusion products. Subsequent decay events *at this position* give not just the decay information of the atom (half-life,  $\alpha$ -particle energy) but also the corresponding information for its decay products, which are recognizable and thus 'known' nuclei. This therefore gives a history of stepwise decay of the initial product.

Thus reaction of  $^{209}\text{Bi}$  with  $^{54}\text{Cr}$  led to very short-lived nuclei ( $t_{1/2} = 4.7$  ms) emitting  $\alpha$ -particles with an energy of 10.38 MeV. This  $\alpha$ -emitter correlated with a decay chain composed of three successive  $\alpha$ -emitters, identified as  $^{258}_{105}$  (4.4 s;  $\alpha$ -particles of 9.17 MeV);  $^{254}_{\text{Lr}}$  (13 s;  $\alpha$ -particles of 8.46 MeV); and  $^{250}_{\text{Md}}$  (52 s;  $\alpha$ -particles of 7.75 MeV). The product of the fusion reaction was thus  $^{262}_{107}$ .



The limiting factor in detecting the reaction product is thus the time of flight of the product from the target to the detector, which is of the order of microseconds.

## 14.7 Predicting Chemistry of the Transactinides

Elements from 104 to 112 are believed to have electron configurations resulting from filling the 6d orbitals, so they are predicted to be transition metals. For the elements with  $Z > 112$ , it is assumed that the 7p orbitals are filled first; elements 119 and 120 involve filling the 8s orbital; whilst from 121 to 153, one electron is first placed in the 7d (or 8p) orbital

then the 5g and 6f orbitals. Relativistic effects (Section 9.7) can cause the elements to have properties differing from those predicted by simple extrapolation.

## 14.8 What is known about the Chemistry of the Transactinides

### 14.8.1 Element 104

The aqua ion of Rf is eluted as the  $\alpha$ -hydroxybutyrate complex from cation-exchange resins much earlier than are trivalent actinides, because it is more weakly adsorbed by the resin, its behaviour resembling that of Zr and Hf. This supports the assignment of a (+4) oxidation state. A coordination number of 6 for  $\text{Rf}^{4+}(\text{aq})$  has been suggested, with a predicted ionic radius of 78 pm for  $\text{Rf}^{4+}$ . It is extracted from concentrated HCl as anionic chloride complexes, unlike trivalent actinides and group I and II metals; these complexes, possibly involving  $\text{Rf Cl}_6^{2-}$ , are eluted from anion-exchange resins with zirconium and hafnium but later than actinides. Like Zr and Hf, however, it forms stable anionic fluoride complexes, and a complex ion  $\text{RfF}_6^{2-}$  has been proposed. The volatility of  $\text{RfCl}_4$  (condensing  $\sim 220^\circ\text{C}$ ) is similar to that of  $\text{ZrCl}_4$  but greater than that of  $\text{HfCl}_4$ ; it is much greater than that of actinide tetrachlorides.  $\text{RfBr}_4$  is more volatile than  $\text{HfBr}_4$  (though the bromide is less volatile than the chloride).

### 14.8.2 Element 105

The aqua ion of Db is readily hydrolysed, even in strong  $\text{HNO}_3$ , and resembles those of  $\text{Nb}^V$ ,  $\text{Ta}^V$  and  $\text{Pa}^V$  rather; the +4 ions of the Group IV elements don't do this, so this is an argument in favour of the +5 oxidation state in aqueous solution. Similarly, elution of Db as the  $\alpha$ -hydroxybutyrate complex from cation-exchange resins shows it to be eluted rapidly, like  $\text{Nb}^V$ ,  $\text{Ta}^V$ , and  $\text{Pa}^V$  but unlike  $\text{Zr}^{4+}$  and  $\text{Eu}^{3+}$  ions, which are strongly retained on the column. Study of complex formation in HCl indicates resemblances to  $\text{Nb}^V$  and  $\text{Pa}^V$  rather than  $\text{Ta}^V$ . It forms anionic fluoride complexes which, like those of Nb, Ta, and Pa, are strongly adsorbed on anion-exchange resins. Study of the volatility of the halides (assumed to be pentahalides) indicates that  $\text{DbBr}_5$  is less volatile than  $\text{NbBr}_5$  and  $\text{TaBr}_5$  (in contradiction of recent theoretical predictions) and  $\text{RfBr}_4$ . The chloride appears to be more volatile than the bromide (at present, it still remains to be confirmed that it was the binary halides studied in these experiments rather than oxyhalides, as well as confirming the oxidation state of the element).

### 14.8.3 Element 106

A comparative study of the reaction of  $^{263}\text{Sg}$ , Mo, and W with  $\text{SOCl}_2$  in air suggests that  $\text{SgCl}_2\text{O}_2$  is formed, with similar volatility to the Mo and W homologues. Investigations of Sg in aqueous solution indicate +6 to be the most stable oxidation state and that it forms neutral or ionic oxo and oxohalide compounds, species possibly including  $[\text{SgO}_4]^{2-}$ ,  $[\text{SgO}_3\text{F}]^-$ , or  $[\text{SgO}_2\text{F}_4]^{2-}$ . Chromatographic study of solutions in very dilute HF indicates the formation of  $\text{SgO}_4^{2-}$ , analogous to  $\text{MoO}_4^{2-}$  and  $\text{WO}_4^{2-}$ . So far, 'seaborgium' behaves as a 6d transition metal, similar to Mo and W, with no evidence for deviations due to relativistic effects and little resemblance to uranium.

## 14.8.4 Element 107

In 2000, chemists synthesized atoms of  $^{267}\text{Bh}$  ( $t_{1/2} \sim 17$  s), using the reaction  $^{22}\text{Ne} (^{249}\text{Bk}, 4n) ^{267}\text{Bh}$ . Atoms recoiling from the back of the berkelium target were absorbed onto carbon particles suspended in a flow of helium gas and transported to a quartz wool trap in an oven at  $1000^\circ\text{C}$ . There the carbon and the nuclear reaction products were reacted with a mixture of  $\text{HCl}$  and  $\text{O}_2$  gases. Some six atoms of bohrium were detected as a volatile oxychloride, believed to be  $\text{BhO}_3\text{Cl}$ , by analogy with  $\text{Tc}$  and  $\text{Re}$ .

## 14.8.5 Element 108

In the only studies so far reported (2005), hassium atoms were oxidized to a very volatile oxide (thought to be  $\text{HsO}_4$  by analogy with  $\text{Ru}$  and  $\text{Os}$  – its absorption enthalpy is comparable with that of  $\text{OsO}_4$ ), and deposited on an  $\text{NaOH}$  surface. Six correlated  $\alpha$ -decay chains of  $\text{Hs}$  were observed and attributed to  $\text{Na}_2[\text{HsO}_4(\text{OH})_2]$ , sodium hassate(VIII), by analogy with osmium, the 5d homologue of  $\text{Hs}$ .

1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104 Rf	105 Ha	106 Sg	107 Ns	108 Hs	109 Mt	110	111	112	(113)	(114)	(115)	(116)	(117)	(118)
(119)	(120)	(121)	(154)	(155)	(156)	(157)	(158)	(159)	(160)	(161)	(162)	(163)	(164)	(165)	(166)	(167)	(168)

LANTHANIDES	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
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ACTINIDES	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr
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SUPER- ACTINIDES	(122)	(123)	(124)	(125)	(126)											(153)
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Figure 14.5

'Future' Periodic Table (reproduced with permission from G.T. Seaborg, *J. Chem. Soc., Dalton Trans.*, 1996, 3904).

## 14.9 And the Future?

Already many more elements have been synthesized than could be predicted in the early 1960s. Higher neutron-flux reactors could make the necessary amounts of the heavier transuranium elements needed for synthesis of the elements beyond 112. Much will depend upon whether the more neutron-rich isotopes with longer half-lives, essential for any study of chemical properties, can be made. The only safe prediction is the unpredictability of this area.

**Question 14.1** Study the electron configurations in Table 14.2, and use your knowledge of the properties of lighter elements to predict properties of the following elements and their compounds:

- (a) Element 104 and its compounds
- (b) Element 106 and its compounds
- (c) Element 111 and its compounds
- (d) Element 114 and its compounds
- (e) Element 118 and its compounds

**Answer (a)** Element 104 falls below Hf in the Periodic Table. It should have the electron configuration  $[\text{Rn}] 5f^{14} 6d^2 7s^2$ . Chemically it should resemble zirconium and hafnium, with a maximum oxidation state of +4, which is likely to be the most stable, though some +3 compounds should exist. It should form an oxide  $\text{MO}_2$  and volatile halides,  $\text{MX}_4$ .

**Answer (b)** Element 106 falls below W in the Periodic Table. It should have the electron configuration  $[\text{Rn}] 5f^{14} 6d^4 7s^2$ . Chemically it should resemble tungsten. It could have oxidation states up to +6, though some have suggested the +4 state might be most likely for the aqua ion. It ought to form some volatile halides, including  $\text{MF}_6$ . It has been suggested that element 106 might form a stable  $\text{M}(\text{CO})_6$ , as do Mo and W.

**Answer (c)** Element 111 falls below Au in the Periodic Table. It should have the electron configuration  $[\text{Rn}] 5f^{14} 6d^9 7s^2$ . Chemically it should resemble gold and be a rather unreactive metal. Its most stable oxidation state is likely to be +3, though there may be a fluoride  $\text{MF}_5$ . It may form an ion  $\text{M}^+$ , analogous to  $\text{Au}^+$ . The oxides may be too unstable to exist at room temperature.

**Answer (d)** Element 114 falls below Pb in the Periodic Table. It should have the electron configuration  $[\text{Rn}] 5f^{14} 6d^{10} 7s^2 7p^2$ . Chemically it should resemble lead. Its most stable oxidation state is likely to be +2, and compounds in the +4 state may be too unstable to exist at room temperature. It should form several compounds, including an oxide  $\text{MO}$  and several halides  $\text{MX}_2$ ; by analogy with lead, the chloride would be insoluble but a nitrate would be soluble. Element 114 could be a rather noble metal (though it has been suggested that the element might be a liquid or even a gas at room temperature!).

**Answer (e)** Element 118 falls below Rn in the Periodic Table. It should have the electron configuration  $[\text{Rn}] 5f^{14} 6d^{10} 7s^2 7p^6$ . Chemically it should resemble radon, but should be the most reactive noble gas (though simple extrapolation of trends down the Group suggests it could be a liquid element at room temperature). It could form compounds in oxidation states including +2 and +4, with fluorides like  $\text{MF}_2$  and  $\text{MF}_4$  as well as a relatively stable chloride  $\text{MCl}_2$ ; because element 118 should be less electronegative than the other noble gases, these compounds might be rather ionic and involatile.

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# Index

Note: Figures and Tables are indicated by *italic page numbers*

- Absorption spectra
  - actinides 202–7
  - lanthanides 64, 68
- Abundance, lanthanides 2–3
- Acetylacetonate complexes
  - lanthanide 39–40, 113
  - scandium 110, 113
- Actinide alkyls 210
- Actinide aqua ions 174
- Actinide aryls 210
- Actinide binary compounds 155–72
- Actinide carbonyls 222
- Actinide complexes
  - coordination numbers 174
  - stability 174–5
- Actinide cyclooctatetraene dianion compounds 219–21
- Actinide cyclopentadienyls 211–15
- Actinide dihalides 167, 168
- Actinide halide complexes 181–3
- Actinide halides 155–69
  - structure types 158–9
  - syntheses 156–8
- Actinide hexahalides 158, 161, 163–4, 166, 167
- Actinide ions, reduction potentials 150–2
- Actinide nitrate complexes 180–1
- Actinide organometallic compounds 209–24
- Actinide oxides 169–70
- Actinide oxyhalides 165–6, 166, 167, 170–1
- Actinide pentahalides 158–9, 161, 165, 166
- Actinide pentamethylcyclopentadienyl compounds 215–18
- Actinide tetrahalides 158, 159, 161–3, 166, 167
- Actinide thiocyanates 183
- Actinide trihalides 157, 158, 158, 163, 166, 167, 168–9
- Actinides
  - characteristics 149–50
  - electron configurations 150
  - ionization energies 151
  - isotopes 147
  - occurrence 145
  - oxidation states 149, 156, 157, 160, 169, 188, 190–1
  - relativistic effects 152
  - synthesis of 145–6
- Actinium
  - chemistry 186–7
  - electron configuration 150
  - ionization energies 151
  - isotope(s) 147, 186
  - metal 186
- Actinium halides 165
- Actinium ion(s)
  - radius 186
  - reduction potential(s) 151, 186
- Adiabatic demagnetization 65
- Alcohols, oxidation of 123
- Alkali metal hydrides, with cerium(III) chloride 130
- Alkenes, oxidation of 123
- Alkoxides
  - lanthanide 48–9, 55, 57, 101
  - as organic catalysts 135
  - scandium 111–12
  - uranium 185, 186
  - yttrium 115
- Alkylamides
  - lanthanide 47–8, 52
  - scandium 111
- Alkyls
  - actinide 210
  - lanthanide 89–90, 99
- Alloys, lanthanide-based 25
- Americium
  - chemistry 195–6
  - electron configuration 150
  - ionization energies 151
  - isotope(s) 147, 195
- Americium complexes 196
- Americium halides 167
- Americium ion(s), reduction potential(s) 151, 195

- Amides
  - reduction of 125–6
  - uranium 184–5
- Ammine complexes
  - lanthanide 43
  - scandium 111
- Aqua ions
  - actinides 174
  - lanthanides 18–19, 37
  - scandium 108–9
- Aqueous stability constants, lanthanide ion(s) 36, 108
- Arene complexes
  - actinide 221–2
  - lanthanide 101–2
- Arenes, oxidation of 121–2
- Aromatic compounds, oxidation of 121–3
- Aryloxides
  - lanthanide 48–9, 55
  - as organic catalysts 134–5
  - uranium 185
- Aryls
  - actinide 210
  - lanthanide 90–1, 100
- Atomic number 1, 115
- Atomic radii, lanthanides 14, 14, 15, 24
- Atomization enthalpies, lanthanides 17
- Attractyligenin, synthesis of 124–5
- Barbier reactions 126
- Barium
  - atomic radius 14
  - atomization enthalpy 17
- Bastnasite (ore) 3, 3
- Berkelium
  - electron configuration 150
  - ionization energies 151
  - isotope(s) 147
- Berkelium ion(s), reduction potential(s) 151
- Berkelium trichloride, absorption spectrum 206–7
- Binary compounds
  - actinides 155–72
  - lanthanides 25–31
- 2,2'-Bipyridyl complexes, lanthanide 43–4
- Bis(cyclopentadienyl) compounds
  - actinide 211, 214
  - lanthanide 92, 100
- Bis(pentamethylcyclopentadienyl) alkyls
  - actinide 215
  - lanthanide 96, 97
- Bis(pentamethylcyclopentadienyl)thorium
  - methyl cation 216–17
- Bohrium (element 107)
  - chemistry 235
  - electron configuration 230
  - isotopes 231
  - synthesis of 228
- Borides, lanthanide 31
- Born–Haber cycles 15
- Bridging ligands, lanthanide cyclopentadienyls 92, 93
- Calcium ions, aqueous stability constants 36
- Californium
  - electron configuration 150
  - ionization energies 151
  - isotope(s) 147
  - synthesis of 146
- Californium halides 168
- Californium ion(s), reduction potential(s) 151
- Carbides, lanthanide 31
- Carbonate complexes, actinide 178, 192, 193
- Carbonyl compounds
  - addition of halogenoalkanes to 126
  - reduction of 124–6, 134–5
- Carbonyls
  - actinide 222
  - lanthanide 102–3
- Carboxylic acids, reduction of 125
- Catalysts
  - actinide compounds as 216–17, 218
  - lanthanide compounds as 127–8, 132, 134–5, 135–8
- Cerium
  - abundance 2, 3
  - atomic radius 14, 15, 25
  - atomization enthalpy 17
  - electron configuration 9, 10, 12
  - ionization energies 12, 13
- Cerium(IV) alkoxides 101
- Cerium(IV) ammonium nitrate (CAN), use in organic chemistry 121, 122, 123
- Cerium(IV) ammonium sulfate (CAS), use in organic chemistry 121, 122
- Cerium bis(cyclooctatetradiendiyl) complex 101
- Cerium(III) chloride
  - with alkali metal hydrides 130
  - uses in organic chemistry 128–30
- Cerium(IV) compounds/complexes 56–7, 101
  - as oxidants 121–3
- Cerium halides 15–17, 16, 26, 27–8, 28, 29
- Cerium ion(s)
  - aqueous stability constants 36
  - colour in aqueous solution 66
  - energy level diagram 63
  - hydration enthalpies 15
  - magnetic moment 65
  - radius 14, 15, 109
  - redox potentials 20
- Cerium oxides 29
- Chemical separation, lanthanides 4

- Chinese rare-earth ores 3  
 Chromium ion(s), radii 109  
 Cobalt ion(s), radii 109  
 Colours in aqueous solution, lanthanide ions 66  
 Complexes  
   lanthanide 37–46  
   stability 35–6  
 Cooper pair (electron pair) 31  
 Coordination chemistry  
   actinides 173–99  
   lanthanides 35–60  
   scandium 108–14  
 Coordination numbers 50–1  
   actinide compounds and complexes 158, 174  
   first-order effects 51  
   formulae and 54  
   lanthanide compounds and complexes 51, 109, 113  
   lanthanide contraction and 53–4  
   scandium 112–14  
   second-order effects 51  
 Copper(II) ions, aqueous stability constants 36  
 Crown ether complexes  
   lanthanide 41–2  
   scandium 109, 110  
 Crystal field (CF) splitting  
   lanthanide ions 66  
   uranium ions 203  
 Curium  
   electron configuration 150  
   ionization energies 151  
   isotope(s) 147  
 Curium(III) chloride 168  
 Curium ion(s), reduction potential(s) 151  
 Cyclooctatetraene dianion compounds  
   actinide 219–21  
   lanthanide 98–9  
   *see also* Uranocene  
 Cyclooctatetraenediyls, lanthanide 100  
 Cyclopentadienyls  
   actinide  
     oxidation state (III) 214–15  
     oxidation state (IV) 211–14  
     oxidation state (V) 211  
     oxidation state (VI) 211  
   lanthanide  
     oxidation state (II) 100  
     oxidation state (III) 91–4  
   scandium 114  
   *see also* Pentamethylcyclopentadienyl compounds  
 d-block metals, compared with lanthanides 7  
 Darmstadtium (element 110) 228, 230, 232  
 Diels–Alder reaction 127  
   hetero-Diels–Alder reaction 128  
   imino-Diels–Alder reaction 133–4  
   lanthanide compounds as catalysts 127–8, 132  
 Dihalides  
   actinide 167, 168  
   lanthanide 17–18, 28–9  
    $\beta$ -Diketonate complexes  
     lanthanide 39–41, 52, 77–8, 127–8  
     as NMR shift reagents 77–8, 127  
   Lewis base adducts 41, 52  
   scandium 110  
 Diphenylphenoxides, lanthanide 49–50  
 Disproportionation  
   lanthanide halides 16, 17  
   neptunium ions in acid solution 190–1  
 Dithiocarbamates, lanthanide 46  
 Dithiophosphates, lanthanide 46  
 Dubnium (element 105)  
   chemistry 234  
   electron configuration 230  
   isotopes 231  
   synthesis of 227  
 Dysprosium  
   abundance 2, 3  
   atomic radius 14, 15, 24  
   atomization enthalpy 17  
   electron configuration 9, 10  
   ionization energies 13  
 Dysprosium halides 16, 26, 28–9, 28  
 Dysprosium ion(s)  
   aqueous stability constants 36  
   colour in aqueous solution 66  
   energy level diagram 63  
   hydration enthalpy 15  
   magnetic moment 65  
   radius 14, 15, 109  
   redox potentials 20  
 EDTA complexes, lanthanide 42–3, 80  
 Einsteinium  
   electron configuration 150  
   ionization energies 151  
   isotope(s) 147  
 Einsteinium(III) chloride 168–9  
 Einsteinium ion(s), reduction potential(s) 151  
 Electromagnetic process  
   transactinides separated by 230, 233  
   uranium isotopes separated by 149, 163–4  
 Electron configurations  
   actinides and ions 150  
   lanthanides and ions 9, 10, 12  
   transactinides 230  
 Electron Paramagnetic Resonance (EPR)  
   spectroscopy, lanthanide ions 82–3



- Electronic spectra
  - actinides 202–7
  - hypersensitive transitions 68–9
  - lanthanide ions 64, 66–9
- Element 112 228, 230, 232
- Element 113 229, 230, 232
- Element 114 228, 230, 232
- Element 115 229, 230, 232
- Element 116 228, 230, 232
- Element 118 228, 229, 230, 232
- Energy level diagrams
  - lanthanide ions 63, 65–6
  - uranium(IV) ion 204
  - uranyl ion 175, 176
- Enthalpy of atomization, lanthanides 17
- Enthalpy changes, lanthanides 14–19
- Enthalpy of formation, lanthanide halides 16
- Enthalpy of hydration, lanthanide ions 15
- Erbium
  - abundance 2, 3
  - aqueous stability constants for  $\text{Ln}^3$  ions 36
  - atomic radius 14, 15, 24
  - atomization enthalpy 17
  - electron configuration 9, 10
  - hydration enthalpy for ion 15
  - ionization energies 13
  - redox potentials of ions 20
- Erbium halides 16, 26
- Erbium ion(s)
  - colour in aqueous solution 66
  - energy level diagram 63
  - magnetic moment 65
  - radius 14, 15, 109
- Euro banknotes 77
- Europium
  - abundance 2, 3
  - atomic radius 14, 14, 15, 23, 24
  - atomization enthalpy 17
  - boiling point of metal 23, 24, 25
  - electron configuration 9, 10
  - ionization energies 12, 13
- Europium aqua ion, stability 19
- Europium complexes
  - electronic spectra 66
  - luminescence 74, 75
  - as NMR shift reagents 77, 78
- Europium halides 16, 26, 28–9, 28
- Europium ion(s)
  - aqueous stability constants 36
  - colour in aqueous solution 66
  - energy level diagram 63
  - hydration enthalpies 15
  - luminescence 70–2, 73
  - magnetic moment 65
  - radius 14, 15, 109
  - redox potential 20
- Europium oxides 29–30
- Extraction, lanthanides 3–4
- f orbitals 10, 11
  - lanthanide properties affected by 10–11
- Fermium
  - chemistry 196–7
  - electron configuration 150
  - ionization energies 151
  - isotope(s) 147
  - synthesis of 146
- Fermium ion(s), reduction potential(s) 151
- Fluorescence, uranyl complexes 202
- Fluorox process 161
- Fractional crystallization, lanthanides 4
- Friedel–Crafts reactions 131
- Gadolinite (ore) 1
- Gadolinium
  - abundance 2, 3
  - atomic radius 14, 15, 24
  - atomization enthalpy 17
  - electron configuration 9, 10, 12
  - ionization energies 12, 13
- Gadolinium complexes, medical applications 45, 78, 80–2
- Gadolinium halides 16, 26, 28, 29
- Gadolinium ion(s)
  - aqueous stability constants 36
  - colour in aqueous solution 66
  - energy level diagram 63
  - EPR spectroscopy 82, 84
  - hydration enthalpy 15
  - magnetic moment 65
  - radius 14, 15, 109
  - redox potentials 20
- Gadolinium texaphyrin 45, 82, 83
- Gas centrifugation, uranium isotopes separated by 148, 164
- Gaseous diffusion, uranium isotopes separated by 148, 164
- Graham's Law of gaseous diffusion 148, 164
- Grob oxidative fragmentation 123
- Ground state(s)
  - actinide ions 202, 203, 204
  - lanthanide ions 62, 65
- Group I metals, compared with lanthanides 7
- Hafnium
  - atomic radius 14
  - atomization enthalpy 17
- Halide complexes
  - actinide 159–60, 181–3, 192
  - lanthanide 44, 46, 56
  - scandium 109

- Halides  
actinide 155–69  
lanthanide 14–18, 25–9  
scandium 108  
yttrium 114  
*see also* Dihalides; Tetrahalides; Trihalides
- Halogen organic compounds, reduction of 124
- Hassium (element 108)  
chemistry 235  
electron configuration 230  
isotopes 231  
synthesis of 228
- Hess's Law 16, 17
- Hetero-Diels–Alder reactions 128
- Hexahalides, actinide 158, 161, 163–4, 166, 167
- Holmium  
abundance 2, 3  
atomic radius 14, 15, 24  
atomization enthalpy 17  
electron configuration 9, 10  
ionization energies 13
- Holmium halides 16, 26, 28
- Holmium ion(s)  
aqueous stability constants 36  
colour in aqueous solution 66  
energy level diagram 63  
hydration enthalpy 15  
magnetic moment 65  
radius 14, 15, 107, 109  
redox potentials 20
- Hund's rules 62
- Hydrated salts  
lanthanide 37–8  
scandium 109
- Hydration enthalpies, lanthanide ions 15
- Hydride cyclopentadienyl complexes, lanthanide 98
- Hydride pentamethylcyclopentadienyl complexes  
actinide 217–18  
lanthanide 98
- Hydrides, lanthanide 31–2
- Hydrogenation catalysts 135–6
- Imino-Diels–Alder reactions 133–4
- Insect traps 76
- International Union of Pure and Applied Chemistry (IUPAC), nomenclature of transactinides 229
- Ion-exchange chromatography, lanthanides 4–5, 6
- Ionic radii, lanthanides 14, 14, 15, 50, 107, 109
- Ionization energies  
actinides 151  
lanthanides 12, 13
- Iron(III) ions, aqueous stability constants 36
- Iron ion(s), radii 109
- Isopropoxides, lanthanide 48–9
- Ketones,  $\alpha$ -heterosubstituted, reduction of 124
- Landé *g*-factor 64
- Lanthanide alkoxides 48–9, 55, 57, 101  
as organic catalysts 135
- Lanthanide alkylamides 47–8, 52
- Lanthanide alkyls 89–90, 99
- Lanthanide alloys 25
- Lanthanide ammine complexes 43
- Lanthanide aqua ions 37, 57  
stability 18–19
- Lanthanide–arene complexes 101–2
- Lanthanide aryloxides 48–9, 55  
as organic catalysts 134–5
- Lanthanide aryls 90–1, 100
- Lanthanide binary compounds 25–31
- Lanthanide bis(cyclopentadienyl) compounds 92
- Lanthanide bis(pentamethylcyclopentadienyl) methyls 96, 97
- Lanthanide borides 31
- Lanthanide carbides 31
- Lanthanide carbonyls 102–3
- Lanthanide complexes 37–46  
coordination numbers 51–4  
luminescence 74–5  
NMR applications 77–82  
stability 35–6
- Lanthanide contraction 7–8, 11–12  
coordination numbers and 53–4  
examples 39
- Lanthanide crown ether complexes 41–2
- Lanthanide cyclooctatetraene dianion compounds 98–9
- Lanthanide cyclooctatetraenediyls 100
- Lanthanide cyclopentadienyls 91–4, 100
- Lanthanide dihalides 28–9  
enthalpies of formation 16  
properties 28–9  
stability 17–18  
structures 28  
syntheses 28
- Lanthanide  $\beta$ -diketonate complexes 39–41, 52  
as Diels–Alder catalysts 127–8  
as NMR shift reagents 77–8, 127
- Lanthanide EDTA complexes 42–3
- Lanthanide halide complexes 44, 46, 56
- Lanthanide halides 25–9  
enthalpies of formation 16  
stability 14–18  
*see also* Dihalides; Tetrahalides; Trihalides
- Lanthanide hydrated salts 37–8

- Lanthanide hydride cyclopentadienyl complexes 98
- Lanthanide hydrides 25, 31–2
- Lanthanide ions
- aqueous stability constants 36, 108
  - colours in aqueous solution 66
  - coordination numbers 51, 109
  - electron configurations 10, 12
  - electronic spectra 65–9
  - energy level diagrams 63, 65–6
  - enthalpies of hydration 15
  - EPR spectroscopy 82–3
  - ground state 62
  - luminescence 69–77
  - magnetic properties 62–5
  - as probes in biological systems 83–4
  - radii 14, 14, 15, 50, 107, 109
  - redox potentials 19, 20, 107
- Lanthanide isopropoxides 48–9, 57
- Lanthanide–lanthanide bonds 103
- Lanthanide metallocenes 98–9
- Lanthanide mono(pentamethylcyclopentadienyl) methyls 96, 97
- Lanthanide N-donor complexes 43–4
- Lanthanide nitrate complexes 41
- Lanthanide nitrides 31
- Lanthanide O-donor complexes 38–9, 56–7
- Lanthanide organometallic compounds 11, 89–105
- organic reactions catalysed by 136–8
  - +2 oxidation state 99–100
  - +3 oxidation state 89–99
  - +4 oxidation state 101
- Lanthanide oxides 29–31
- superconducting oxides 30–1
- Lanthanide oxysulfides 32
- Lanthanide pentamethylcyclopentadienyls 94–5
- Lanthanide phosphors (TV displays) 75–6, 114
- Lanthanide S-donor complexes 46
- Lanthanide shift reagents (LSRs) 77
- Lanthanide silylamides 47, 52, 83
- Lanthanide sulfides 32
- Lanthanide tetrahalides 27–8
- enthalpies of formation 16
  - stability 14–17
- Lanthanide thiolates 50
- Lanthanide triflates, uses in organic chemistry 131–4
- Lanthanide trihalides 25–7
- enthalpies of formation 16
  - properties 27
  - structures 26–7
  - syntheses 25–6
- Lanthanides
- abundance 2, 3
  - atomic radii 14, 14, 15, 24
  - atomization enthalpies 17
  - characteristics 2
  - compared with d-block and s-block metals 7
  - coordination chemistry 35–60
    - (+2) oxidation state 55
    - (+4) oxidation state 56–7  - early history 1–2
  - electron configurations 9, 10, 12
  - elements/metals, properties 23–4
  - enthalpy changes for formation of compounds 14–19
  - extraction 3–4, 24–5
  - ionic radii 14, 15, 50, 107, 109
  - ionization energies 12, 13
  - metals
    - boiling points 23, 24, 25
    - extraction/synthesis of 24–5
    - in organic chemistry 135–6
    - properties 23–4, 25
    - uses 25  - occurrence in various ores 3
  - organometallic chemistry 11
  - oxidation states 10, 14, 18, 29
  - position in Periodic Table 1, 2, 6–7
  - separation of 4–6
- Lanthanum
- abundance 2, 3
  - atomic radius 14, 15, 24
  - atomization enthalpy 17
  - boiling point of metal 24, 25
  - electron configuration 9, 10, 12
  - ionization energies 13
- Lanthanum aqua ion, stability 19
- Lanthanum boride 31
- Lanthanum compounds/complexes, coordination numbers 113
- Lanthanum halides 15–16, 16, 26, 28, 29
- Lanthanum ion(s)
- aqueous stability constants 36, 108
  - colour in aqueous solution 66
  - hydration enthalpy 15
  - magnetic moment 65
  - radius 14, 15, 109, 186
  - redox potential(s) 20, 107, 186
- Lanthanum–nickel alloys 25, 31, 135
- Lanthanum nickel hydrides 25, 31, 136
- Lasers
- lanthanide ions in 76–7
  - uranium isotopes separated using 149, 164, 165
- Lawrencium
- electron configuration 150
  - ionization energies 151
  - isotope(s) 147, 225

- Lawrencium ion(s), reduction potential(s) 151
- Lighting applications, lanthanide ions 76
- Lithium aluminium hydride, with cerium(III) chloride 130
- Luminescence
- Euro banknotes 77
  - lanthanide ions/complexes 69–77
    - ‘antenna’ effects 73, 74
    - applications to sensory probes 74–5
    - in lasers 76–7
    - lighting applications 76
    - quenching 73
    - television phosphors 75–6
- Lutetium
- abundance 2, 3
  - atomic radius 14, 15, 24
  - atomization enthalpy 17
  - electron configuration 9, 10, 12
  - ionization energies 12, 13
- Lutetium compounds/complexes, coordination numbers 113
- Lutetium halides 16, 26
- Lutetium ion(s)
- aqueous stability constants 36, 108
  - colour in aqueous solution 66
  - hydration enthalpy 15
  - magnetic moment 65
  - radius 14, 15, 109
  - redox potential(s) 20, 107
- Magnetic moments, lanthanide ions 64–5
- Magnetic properties
- lanthanide ions 62–5
  - uranium compounds 207–8
- Magnetic resonance imaging (MRI)
- 78–9
  - contrast agents 45, 79–81
- Manhattan project 4, 149, 163
- Mannich reactions 132–3
- Medical applications, lanthanide compounds 45, 78, 80–2
- Meerwein–Ponndorf–Verley reaction 135
- Meitnerium (element 109), electron configuration 228, 230, 231
- Mendelevium
- electron configuration 150
  - ionization energies 151
  - isotope(s) 147
- Mendelevium ion(s), reduction potential(s) 151
- Metal organic chemical vapour deposition (MOCVD) applications 57
- Metallacycles, actinide 215, 216, 219
- Metallic properties
- actinides 186, 187, 188
  - lanthanides 23–4
- Metallocenes
- actinide 219–21
  - lanthanide 98–9
- Mischmetal 25, 32
- in organic reactions 124, 135
- Monazite (ore) 3, 3, 4, 145
- Mono(pentamethylcyclopentadienyl) complexes
- actinide 216
  - lanthanide 96, 97
- N-donor complexes
- lanthanide 43–4
  - scandium 112
- Neodymium
- abundance 2, 3
  - atomic radius 14, 15, 24
  - atomization enthalpy 17
  - electron configuration 9, 10
  - ionization energies 13
- Neodymium halides 16, 26, 28–9, 28
- Neodymium ion(s)
- aqueous stability constants 36
  - colour in aqueous solution 66
  - energy level diagram 63
  - hydration enthalpy 15
  - magnetic moment 65
  - radius 14, 15, 109
  - redox potentials 20
- Neodymium lasers 76–7
- Neptunium
- electron configuration 150
  - ionization energies 151
  - isotope(s) 147, 188
- Neptunium complexes 188–9
- Neptunium halides 166
- Neptunium ion(s), reduction potential(s) 151, 188
- Neptunium oxyhalides 166, 171
- Nickel/lanthanide hydride batteries 25, 31
- Nitrate complexes
- actinide 180–1, 193
  - lanthanide 41
  - scandium 110
- Nitrides, lanthanide 31
- Nitriles, reduction of 125–6
- NMR applications, lanthanide complexes 77–82
- Nobelium
- chemistry 196–7
  - electron configuration 150
  - ionization energies 151
  - isotope(s) 147
- Nobelium ion(s), reduction potential(s) 151
- Nuclear waste
- disposal of 194
  - processing of 179–80

- O-donor complexes
  - lanthanide 38–9
  - scandium 109–10
- Occurrence
  - actinides 145
  - lanthanides 2–3
- Ores
  - actinide-containing 145, 148
  - lanthanide-containing 1, 3
- Organic chemistry 121–43
- Organocerium compounds 128–9
- Organometallic compounds
  - actinide 209–24
  - lanthanide 11, 89–105, 136–8
- Oxidation, organic compounds 121–3
- Oxidation states
  - actinides 149, 156, 157, 160, 169, 188, 190–1
  - lanthanides 10, 14, 18, 29
- Oxide superconductors 30–1, 114
- Oxides
  - actinide 169–70
  - lanthanide 29–31
  - scandium 108
- Oxyhalides, actinide 165–6, 166, 167, 170–1
- Oxysulfides, lanthanide 32
- Paramagnetic compounds 62, 207
- Pentahalides, actinide 158–9, 161, 165, 166
- Pentamethylcyclopentadienyl compounds
  - actinide
    - cationic alkyls 216–17
    - oxidation state (III) 218
    - oxidation state (IV) 215–18
  - lanthanide 94–5
  - scandium 114
- Perchlorate complexes, lanthanide 44
- Periodic Table 1, 2, 6–7, 107, 115
  - future developments 235
- 1,10-Phenanthroline complexes, lanthanide 43–4
- Phosphide complexes, lanthanide 50
- Phthalocyanine complexes 45, 178–9
- Pinacols 125
- Pitchblende (ore) 145, 148
- Plutonium
  - aqueous chemistry 189–90
  - coordination chemistry 191–3
  - electron configuration 150
  - environmental considerations 193–4
  - ionization energies 151
  - isotope(s) 147
  - oxidation states 190–1
- Plutonium carbonate complexes 192, 193
- Plutonium halide complexes 192
- Plutonium halides 166–7
- Plutonium ion(s)
  - radii 109
  - reduction potential(s) 151, 190
- Plutonium nitrate complexes 193
- Plutonium oxyhalides 167, 171
- Plutonium triflates 193
- Porphyrins and related compounds
  - lanthanide 44–5
  - scandium 112
  - uranyl 178
- Praseodymium
  - abundance 2, 3
  - atomic radius 14, 15, 24
  - atomization enthalpy 17
  - electron configuration 9, 10
  - ionization energies 12, 13
- Praseodymium halides 16, 26, 27–8, 28, 29
- Praseodymium ion(s)
  - aqueous stability constants 36
  - colour in aqueous solution 66
  - electronic absorption spectra 64, 66
  - energy level diagram 63
  - hydration enthalpy 15
  - magnetic moment 65
  - radius 14, 15, 109
  - redox potentials 20
- Praseodymium oxides 29
- Promethium 115–17
  - abundance 2, 3, 115
  - atomic radius 14, 15, 25
  - electron configuration 9, 10
  - ionization energies 13
  - isotopes 115–16
- Promethium halides 16, 26, 116
- Promethium hydrated salts 116–17
- Promethium ion(s)
  - aqueous stability constants 36
  - colour in aqueous solution 66
  - energy level diagram 63
  - hydration enthalpy 15
  - magnetic moment 65
  - radius 14, 15, 109
  - redox potentials 20
- Promethium oxide 116
- Protactinium
  - chemistry 187–8
  - electron configuration 150
  - extraction of 148
  - ionization energies 151
  - isotope(s) 147, 187
  - metal 187
- Protactinium halide complexes 187
- Protactinium halides 158–9, 165
- Protactinium ion(s), reduction potential(s) 151
- Protactinium oxyhalides 165–6, 170–1
- Pyridine complexes, lanthanide 43

- Radioactive lanthanide isotopes, separation from uranium 4
- Redox/reduction potentials
  - actinide ions 150–2, 188, 195
  - lanthanide ions 19, 20, 107
- Reduction, organic compounds 124–7, 134–5
- Reformatsky reactions 127
- Relativistic effects 152, 234
- Roentgenium (element 111) 228, 230, 232
- Russell-Saunders coupling scheme 61, 201
- Rutherfordium (element 104)
  - chemistry 234
  - electron configuration 230
  - isotopes 231
  - synthesis of 227
- s-block metals, compared with lanthanides 7
- Samarium
  - abundance 2, 3
  - atomic radius 14, 15, 24
  - atomization enthalpy 17
  - boiling point of metal 23, 24, 25
  - electron configuration 9, 10
  - ionization energies 13
- Samarium halides 16, 26, 28–9, 28
- Samarium(II) iodide
  - as reducing agent 124–7
  - synthesis of 124
- Samarium ion(s)
  - aqueous stability constants 36
  - colour in aqueous solution 66
  - energy level diagram 63
  - hydration enthalpies 15
  - magnetic moment 65
  - radius 14, 15, 109
  - redox potentials 20
  - term symbol for ground state 62
- Samarium oxides 30
- Samarium(II) pentamethylcyclopentadienyl 100
  - reactions 100, 101
- Samarium(III) pentamethylcyclopentadienyl 94, 95
- Samarium sulfide 32
- Scandium 107–14
  - metal 108
- Scandium alkoxides 111–12
- Scandium alkylamides 111
- Scandium aqua ions 108–9, 113
- Scandium compounds/complexes, coordination numbers 112–14
- Scandium crown ether complexes 109, 110
- Scandium cyclopentadienyls 114
- Scandium halide complexes 109
- Scandium halides 108, 113
- Scandium hydrated salts 109
- Scandium ion(s)
  - aqueous stability constants 36, 108
  - coordination number(s) 109, 109, 113
  - radius 107, 109
  - redox potential(s) 107
- Scandium O-donor complexes 109–10
- Scandium organometallic compounds 114
- Scandium oxide 108, 113
- Scandium silylamide 111
- Scandium triflate, uses in organic chemistry 131, 132
- Seaborgium (element 106)
  - chemistry 234
  - electron configuration 230
  - isotopes 231
  - synthesis of 228
- Separation, lanthanides 4–6
- Siderophore complexes, plutonium in 194, 195
- SILEX system 164
- Silylamides
  - lanthanide 47, 52
  - scandium 111
- Sodium borohydride, with cerium(III) chloride 130
- Solvent extraction, lanthanides 5–6
- Stability constants, lanthanide ions in aqueous solution 36, 108
- Sulfides, lanthanide 32
- Superconductors, lanthanide oxides 30–1, 114
- Supercritical carbon dioxide, use in separation method 6
- Television displays, phosphors in 75–6, 114
- Terbium
  - abundance 2, 3
  - atomic radius 14, 15, 24
  - atomization enthalpy 17
  - electron configuration 9, 10
  - ionization energies 12, 13
- Terbium complexes, luminescence 74–5
- Terbium halides 16, 26, 27–8
- Terbium ion(s)
  - aqueous stability constants 36
  - colour in aqueous solution 66
  - energy level diagram 63
  - hydration enthalpy 15
  - luminescence 70, 71
  - magnetic moment 65
  - radius 14, 15, 109
  - redox potentials 20
- Terbium oxides 29
- Tetra(cyclopentadienyl)actinide compounds 211–12
- Tetrahalides
  - actinide 158, 159, 161–3, 165, 166
  - lanthanide 14–17, 27–8

- Texaphyrins, lanthanide 45, 81–2, 83  
 Thiocyanates  
   actinide 183  
   lanthanide 43, 44, 52, 53  
 Thiolates  
   lanthanide 46, 50  
   uranium 184  
 Thoracene, half-sandwich compound 221  
 Thorium  
   electron configuration 150  
   extraction of 147  
   ionization energies 150, 151  
   isotope(s) 147  
   reactions 156  
 Thorium(IV) bis(pentamethylcyclopentadienyl)  
   methyl cation 216–17  
 Thorium halides 159–60  
 Thorium ion(s)  
   aqueous stability constants 36, 175  
   reduction potential(s) 150, 151  
 Thorium nitrate complexes 180, 181  
 Thorium(IV) oxide 169  
 Thorium oxyhalides 170  
 Thortveitite (ore) 107  
 Thulium  
   abundance 2, 3  
   atomic and ionic radii 14  
   atomic radius 14, 15, 24  
   atomization enthalpy 17  
   electron configuration 9, 10  
   ionization energies 13  
 Thulium halides 16, 26, 28–9, 28  
 Thulium ion(s)  
   aqueous stability constants 36  
   colour in aqueous solution 66  
   energy level diagram 63  
   hydration enthalpy 15  
   magnetic moment 65  
   radius 14, 15, 109  
   redox potentials 20  
 Titanium ion(s), radii 109  
 Transactinides 225–36  
   attempts to isolate 226  
   chemistry 234–5  
   electron configurations 230  
   future developments 235, 236  
   identification of elements 230, 233  
   isotopes, half-lives and decay modes 231–2  
   nomenclature 229  
   prediction of chemistry 233–4  
   stability considerations 225–6  
   synthesis of 226–9  
 Transition metals, compared with lanthanides 7  
 Tributyl phosphate, in nuclear waste processing 179, 180  
 Tricolour lamps 76  
 Trihalides  
   actinide 156, 157, 158, 165, 166, 167, 168–9  
   lanthanide 16, 25–7  
 Triphenylscandium 114  
 Tris(cyclopentadienyl) compounds  
   actinide 214–15  
   lanthanide 92, 93  
 Tris(cyclopentadienyl)uranium chloride,  
   reactions 212, 213  
 Tris(pentamethylcyclopentadienyl) systems  
   samarium compound 94–5  
   uranium compound 219  
 Uraninite (ore) 148  
 Uranium  
   electron configuration 150  
   extraction of 148  
   other elements obtained from 107, 148  
   fission products, lanthanides separated from 4  
   ionization energies 151  
   isotope(s) 147  
   separation of 148–9  
   oxidation states 157, 160  
   reactions 156  
 Uranium alkoxides 185, 186  
 Uranium amides 184–5  
 Uranium(III) bis(pentamethylcyclopentadienyl)  
   chloride 218  
 Uranium compounds, magnetic properties 207–8  
 Uranium halide complexes 181–3  
   temperature-dependent magnetic susceptibility 208  
 Uranium halides 160–3  
 Uranium hexafluoride  
   isotope separation using 163–4, 165  
   synthesis of 161  
 Uranium hydride 170  
 Uranium imides 211, 212  
 Uranium ion(s)  
   aqueous stability constants 36  
   reduction potential(s) 151, 174  
 Uranium nitrate complexes 179, 180–1  
 Uranium oxides 169–70  
 Uranium oxyhalides 171  
 Uranium thiolates 184  
 Uranocene 219–20  
   bonding in 221  
 Uranyl acetate 178  
 Uranyl alkoxides 185  
 Uranyl carbonate complexes 178  
 Uranyl complexes 175–7  
   coordination numbers 177  
   fluorescence 202  
   structures 177, 178

- Uranyl ion ( $\text{UO}_2^{2+}$ )  
  absorption spectra 202, 203  
  aqueous stability constants 36, 175  
  bonding in 175, 176  
  energy level diagram 175, 176  
Uranyl nitrate 179  
  in nuclear waste processing 180  
  solubility in various solvents 179  
Uranyl 'superphthalocyanine' complex 178–9
- Vanadium ion(s), radii 109
- Xenotime (ore) 3, 3
- Ytterbium  
  abundance 2, 3  
  atomic radius 14, 14, 15, 23, 24  
  atomization enthalpy 17  
  boiling point of metal 23, 24, 25  
  electron configuration 9, 10  
  ionization energies 12, 13  
Ytterbium halides 16, 26, 28–9, 28
- Ytterbium ion(s)  
  aqueous stability constants 36  
  colour in aqueous solution 66  
  energy level diagram 63  
  hydration enthalpies 15  
  magnetic moment 65  
  radius 14, 15, 109  
  redox potentials 20
- Yttria 1
- Yttrium 114–15  
  abundance 2, 3  
  electron configuration 10  
  ionization energies 13
- Yttrium alkoxides 115
- Yttrium aluminium garnet (YAG) 76
- Yttrium compounds 114–15
- Yttrium halides 114
- Yttrium ion(s)  
  aqueous stability constants 36, 108  
  hydration enthalpy 15  
  radius 107, 109  
  redox potential(s) 20, 107
- Yttrium oxide superconductors 30–1, 114

*With kind thanks to Paul Nash for creation of the index.*



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# *Química Orgánica*

*Recopilación*

*José A. - UH NMSM*



2009

# *Química Orgánica*

## *Recopilación*

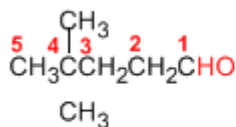
## *Índice.*

- i. Nomenclatura de Aldehídos y Cetonas*
- ii. Preparación de Aldehídos y Cetonas*
- iii. Formación de Hidratos*
- iv. Formación de Hemiacetales*
- v. Formación de Acetales*
- vi. Formación de Acetales Cíclicos*
- vii. Acetales Como Grupos Protectores*
- viii. Formación de Iminas*
- ix. Formación de Oximas*
- x. Formación de Hidrazonas*
- xi. Formación de Azinas*
- xii. Formación de Semicarbazonas*
- xiii. Ensayo de la 2,4 - Dinitrofenilhidrazina*
- xiv. Formación de Cianhídrinas*
- xv. Reacción de Wittig*
- xvi. Oxidación de Baeyer Villiger*
- xvii. Problemas Nomenclatura Aldehídos y Cetonas*
- xviii. Problemas Resueltos de Aldehídos y Cetonas*
- xix. Teorías de Enoles y Enolatos*

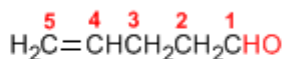
## Nomenclatura de Aldehídos y Cetonas

Los aldehídos se nombran reemplazando la terminación **-ano** del alcano correspondiente por **-al**. No es necesario especificar la posición del grupo aldehído, puesto que ocupa el extremo de la cadena (localizador 1).

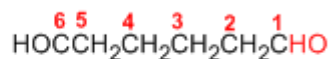
Cuando la cadena contiene dos funciones aldehído se emplea el sufijo **-dial**.



4,4-Dimetilpentanal

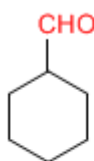


Hex-4-enal

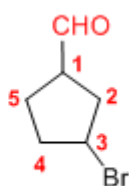


Pentanodial

El grupo **-CHO** unido a un ciclo se llama **-carbaldehído**. La numeración del ciclo se realiza dando localizador 1 al carbono del ciclo que contiene el grupo aldehído.



Ciclohexanocarbaldehído

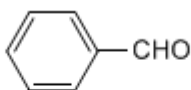


3-Bromociclopentanocarbaldehído

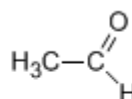
Algunos nombres comunes de aldehídos aceptados por la IUPAC son:



Formaldehído  
(Metanal)

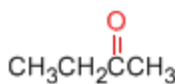


Benzaldehído  
(Bencenocarbaldehído)

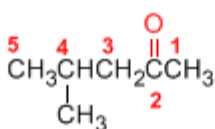


Acetaldehído  
(Etanal)

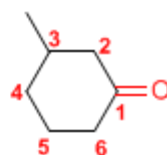
Las cetonas se nombran sustituyendo la terminación **-ano** del alcano con igual longitud de cadena por **-ona**. Se toma como cadena principal la de mayor longitud que contiene el grupo carbonilo y se numera para que éste tome el localizador más bajo.



Butanona

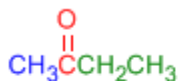


4-Metil-2-pentanona

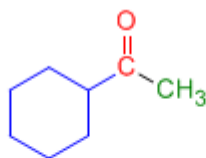


3-Metilciclohexanona

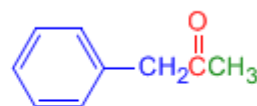
Existe un segundo tipo de nomenclatura para las cetonas, que consiste en nombrar las cadenas como sustituyentes, ordenándolas alfabéticamente y terminando el nombre con la palabra **cetona**.



Etil metil cetona



Ciclohexil metil cetona



Fenil metil cetona

[Siguiete >](#)

[\[Volver\]](#)

## Charles Friedel (1832 - 1899)



**Origen:** Químico frances..

**Lugar de nacimiento:** Estrasburgo.

**Formación:** estudió química en la Universidad de Berlín entre 1895 y 1899, consiguiendo el doctorado este año.

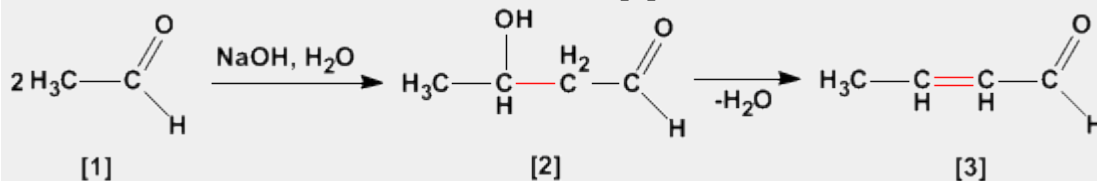
**Docencia:** Profesor en la Universidad de la Sorbona.

**Investigación:** Obtuvo el alcohol propílico. En 1877, Friedel y Crafts describieron por primera vez la reacción del benceno con un haloalcano en presencia de un ácido de Lewis. Esta reacción produce la alquilación del benceno y se conoce como alquilación de Friedl-Crafts.

**Premio Nobel:**

## Aldólica (Condensación)

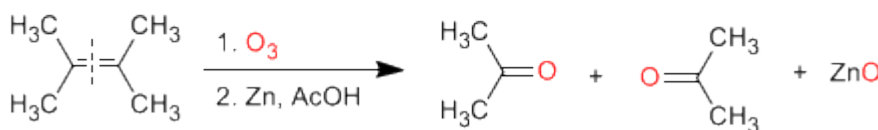
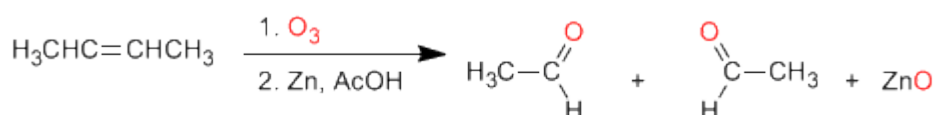
La condensación aldólica es una reacción de aldehídos o cetonas **[1]** que forma 3-hidroxicarbonilos (aldoles) **[2]**. El 3-hidroxialdehído **[2]** bajo condiciones de deshidratación por calentamiento rinde un aldehído alfa,beta-insaturado **[3]**.



## Preparación de aldehídos y cetonas

Los aldehídos y cetonas pueden ser preparados por oxidación de alcoholes, ozonólisis de alquenos, hidratación de alquinos y acilación de Friedel-Crafts como métodos de mayor importancia.

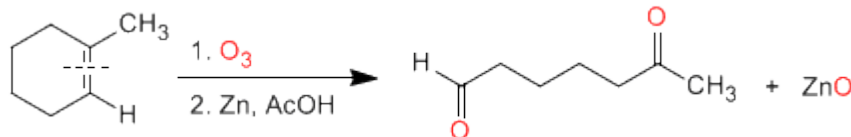
a) **Ozonólisis de alquenos:** Los alquenos rompen con ozono formando aldehídos y/o cetonas. Si el alqueno tiene hidrógenos vinílicos da aldehídos. Si tiene dos cadenas carbonadas forma cetonas.



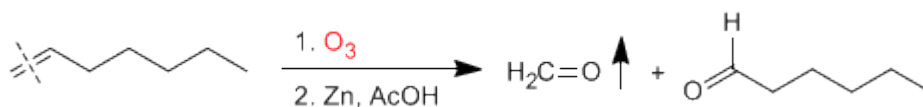
### Ozonólisis

Los alquenos simétricos y terminales permiten la preparación de carbonilos mediante ozonólisis

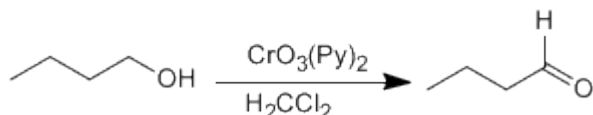
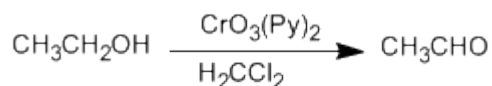
La ozonólisis de alquenos cíclicos produce compuestos dicarbonílicos:



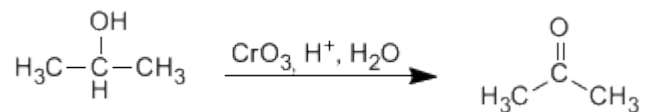
Los alquenos terminales rompen formando metanal, que se separa fácilmente de la mezcla por su bajo punto de ebullición.



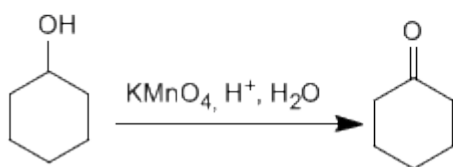
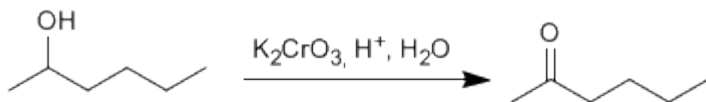
b) **Oxidación de alcoholes:** Los alcoholes primarios y secundarios se oxidan para dar aldehídos y cetonas respectivamente. Deben tomarse precauciones en la oxidación de alcoholes primarios, puesto que sobreoxidan a ácidos carboxílicos en presencia de oxidantes que contengan agua. En estos caso debe trabajarse con reactivos anhidros, como el clorocromato de piridino en diclorometano (PCC), a temperatura ambiente.



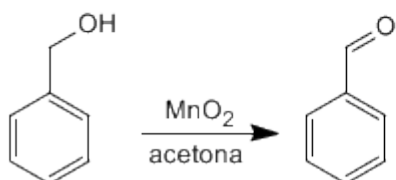
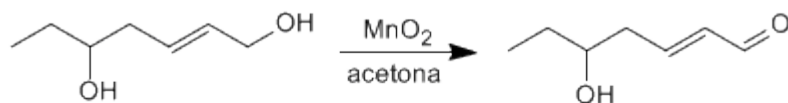
Los alcoholes secundarios dan cetonas por oxidación. Se emplean como oxidantes permanganato, dicromato, trióxido de cromo.



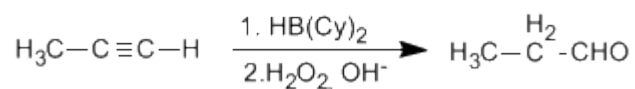
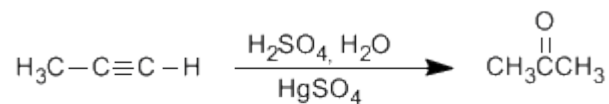
La oxidación supone la pérdida de dos hidrógenos del alcohol. Los alcoholes terciarios no pueden oxidar puesto que carecen de hidrógeno sobre el carbono.



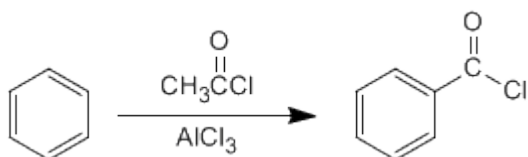
Los alcoholes alílicos y bencílicos se transforman en aldehídos o cetonas por oxidación con dióxido de manganeso en acetona. Esta reacción tiene una elevada selectividad y no oxida alcoholes que no se encuentren en dichas posiciones.



c) **Hidratación de alquinos:** Los alquinos se pueden hidratar Markovnikov, formando cetonas, o bien antiMarkovnikov, para formar aldehídos.



d) **Acilación de Friedel-Crafts:** La introducción de grupos acilo en el benceno permite la preparación de cetonas con cadenas aromáticas.



### Otto Paul Hermann Diels (1876 - 1954)



**Origen:** Químico alemán.

**Lugar de nacimiento:** Königshütte (hoy Chorzów, Polonia).

**Formación:** estudió química en la Universidad de Berlín entre 1895 y 1899, consiguiendo el doctorado este año.

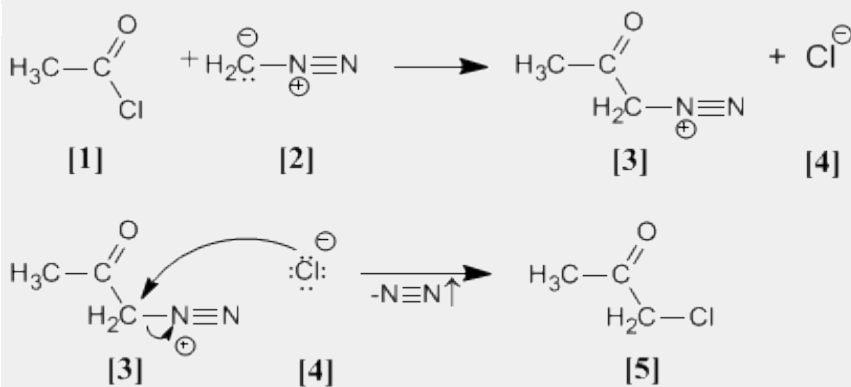
**Docencia:** profesor y jefe del departamento de química en la Universidad de Berlín. En 1916, tomó el puesto de profesor de Química en la Universidad de Kiel, cargo que no dejó hasta su jubilación en 1945.

**Investigación:** En 1906 descubrió el anhídrido malónico. Investigó en reacciones de deshidrogenación con selenio. Síntesis de  $\alpha$ -dicetonas. Pero su trabajo más importante es la reacción de Diels - Alder.

**Premio Nobel:** En 1950 recibió el Premio Nobel junto a Kurt Alder

### Arndt Eistert (Síntesis)

Cloruro de acetilo [1] se trata con diazometano [2] rindiendo la sal de diazonio [3]. El cloruro [4] producido reacciona con la sal de diazonio para dar la  $\alpha$ -clorocetona [5].



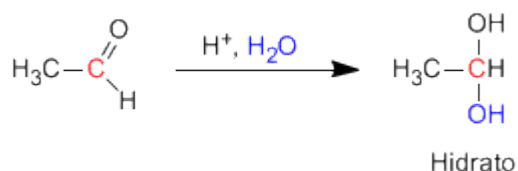
#### Síntesis de Arndt Eistert

Esta reacción permite transformar haluros de alcanoilo en cetonas halogenadas en su posición alfa.



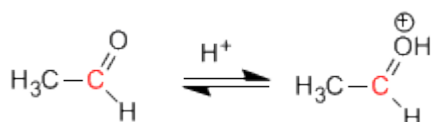
## Formación de Hidratos

Los aldehídos y cetonas reaccionan en medio ácido acuoso para formar hidratos. El mecanismo consta de tres etapas. La primera y más rápida consiste en la protonación del oxígeno carbonílico. Esta protonación produce un aumento de la polaridad sobre el carbono y favorece el ataque del nucleófilo. En la segunda etapa el agua ataca al carbono carbonilo, es la etapa lenta del mecanismo. En la tercera etapa se produce la desprotonación del oxígeno formándose el hidrato final.

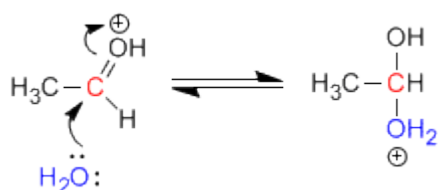


### Mecanismo de la reacción

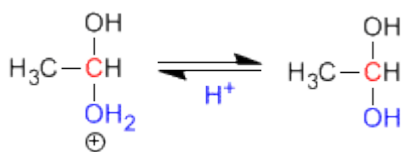
Etapa 1. Protonación del oxígeno carbonílico.



Etapa 2. Ataque nucleófilo del agua al carbonilo protonado.



Etapa 3. Desprotonación del hidrato





**Origen:** Químico estadounidense.

**Lugar de nacimiento:** Budapest

**Formación:** Se doctoró en la Universidad de Budapest en 1949

**Docencia:** Trabajó en el departamento de química orgánica de la Academia de Ciencias de Hungría y posteriormente en la Universidad de Cleveland.

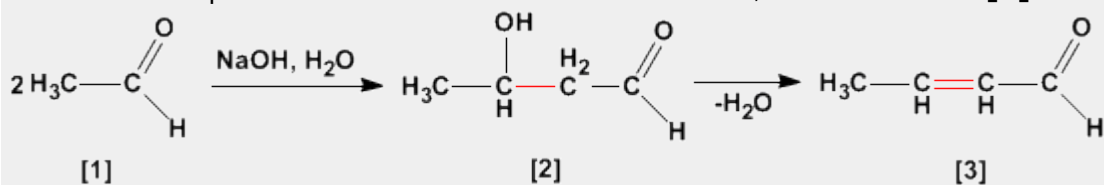
**Industria:** Trabajó en los laboratorios de la Dow Chemical de Ontario

**Investigación:** Olah consiguió preparar carbocationes estables utilizando componentes extremadamente ácidos.

**Premio Nobel:** En 1994 obtuvo el premio Nobel de Química por sus investigaciones sobre los carbocationes

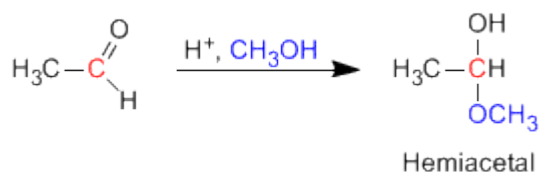
### Aldólica (Condensación)

La condensación aldólica es una reacción de aldehídos o cetonas **[1]** que forma 3-hidroxicarbonilos (aldoles) **[2]**. El 3-hidroxialdehído **[2]** bajo condiciones de deshidratación por calentamiento rinde un aldehído alfa,beta-insaturado **[3]**.



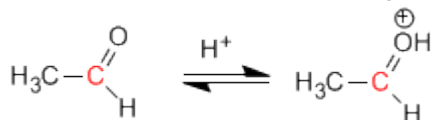
## Formación de Hemiacetales

Los hemiacetales se forman por reacción de un equivalente de alcohol con el grupo carbonilo de un aldehído o cetona. Esta reacción se cataliza con ácido y es equivalente a la formación de hidratos.

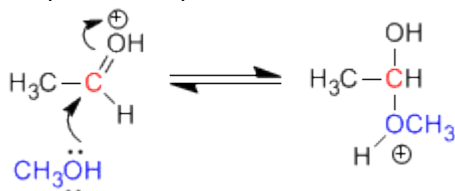


### Mecanismo de la reacción:

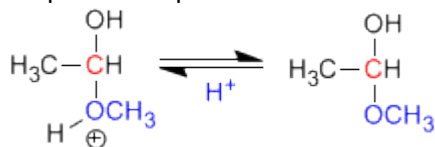
Etapas 1. Protonación del oxígeno carbonílico.



Etapas 2. Ataque nucleófilo del metanol al carbonilo protonado.



Etapas 3. Desprotonación del hemiacetal



### Otto Paul Hermann Diels (1876 - 1954)



**Origen:** Químico alemán.

**Lugar de nacimiento:** Königshütte (hoy Chorzów, Polonia).

**Formación:** estudió química en la Universidad de Berlín entre 1895 y 1899, consiguiendo el doctorado este año.

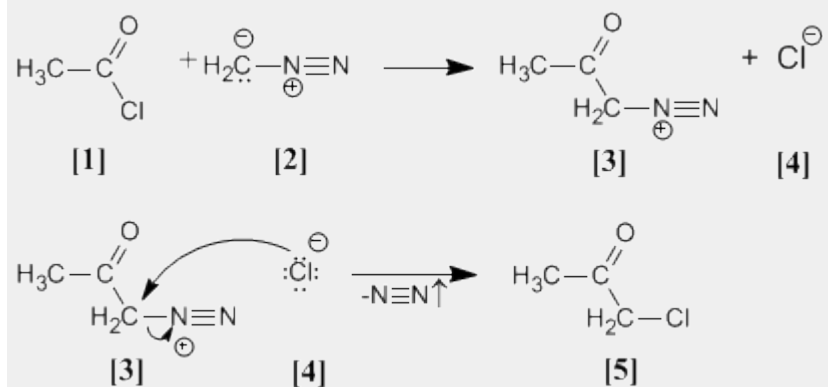
**Docencia:** profesor y jefe del departamento de química en la Universidad de Berlín. En 1916, tomó el puesto de profesor de Química en la Universidad de Kiel, cargo que no dejó hasta su jubilación en 1945.

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**Premio Nobel:** En 1950 recibió el Premio Nobel junto a Kurt Alder

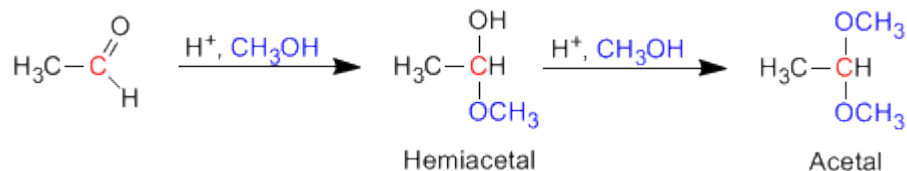
### Arndt Eistert (Síntesis)

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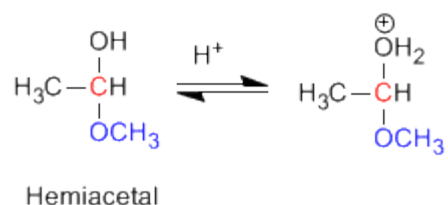
## Formación de Acetales

Los aldehídos y cetonas reaccionan con alcoholes bajo condiciones de catálisis ácida, formando en una primera etapa hemiacetales, que posteriormene evolucionan por reacción con un segundo equivalente de alcohol a acetales.

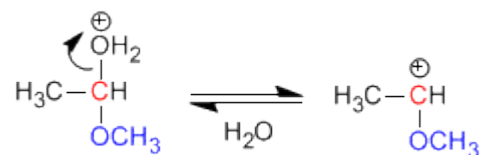


### Mecanismo para la formación de acetales

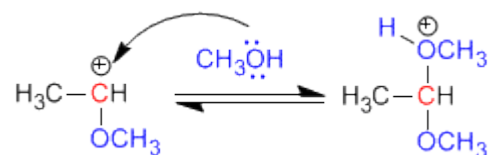
Etapa 1. Protonación del grupo hidroxilo



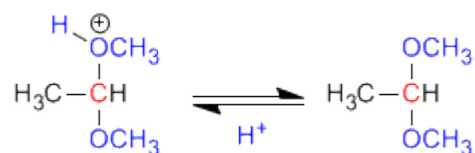
Etapa 2. Pérdida de agua.



Etapa 3. Ataque del alcohol al carbocatión



Etapa 4. Desprotonación del acetal



### Otto Paul Hermann Diels (1876 - 1954)



**Origen:** Químico alemán.

**Lugar de nacimiento:** Königshütte (hoy Chorzów, Polonia).

**Formación:** estudió química en la Universidad de Berlín entre 1895 y 1899, consiguiendo el doctorado este año.

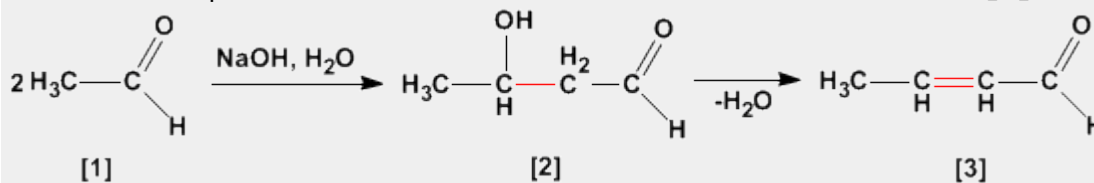
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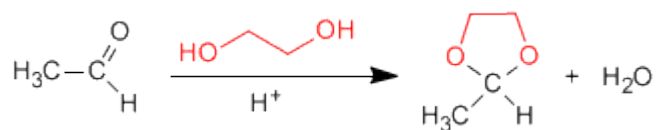
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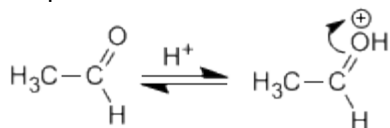
## Formación de acetales cíclicos

Los 1,2- y 1,3-dioles reaccionan con aldehídos y cetonas formando acetales cíclicos. Los equilibrios se desplazan hacia el producto final eliminando el agua formada por destilación azeotrópica con benceno o tolueno.

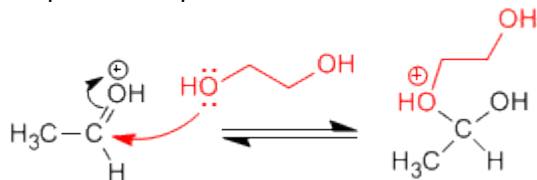


### Mecanismo para la formación de acetales cíclicos:

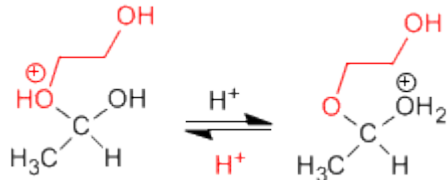
Etapa 1. Protonación del carbonilo



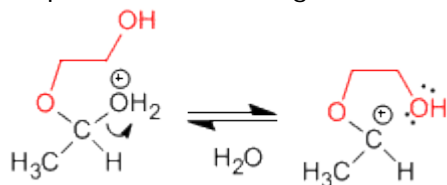
Etapa 2. Ataque nucleófilo del diol al carbonilo.



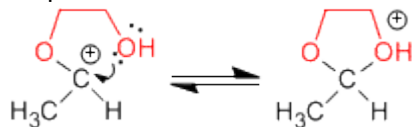
Etapa 3. Equilibrio ácido base entre el éter y el alcohol



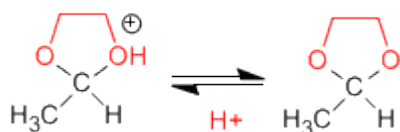
Etapa 4. Pérdida de agua



Etapa 5. Ciclación



Etapa 6. Desprotonación del acetal cíclico



### Kurt Alder (1902 - 1958)



**Origen:** Químico alemán.

**Lugar de nacimiento:** Königshütte (hoy Chorzów, Polonia).

**Formación:** estudió en la Universidad de Kiel. Bajo la supervisión del químico alemán Otto Diels, su jefe e instructor en Kiel.

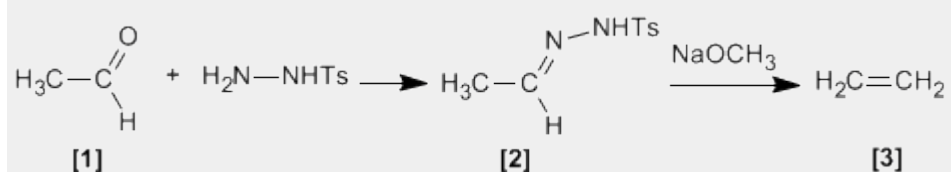
**Docencia:** Alder ejerció como profesor de química en las universidades de Kiel y Colonia.

**Investigación:** Alder se especializó en la síntesis diénica (conocida más tarde como la reacción Diels - Alder) que consiste fundamentalmente en el análisis y formación de compuestos orgánicos complejos. Ya en 1928 ambos fueron coautores de un ensayo sobre este proceso.

**Premio Nobel:** En 1950 recibió el Premio Nobel junto a Diels

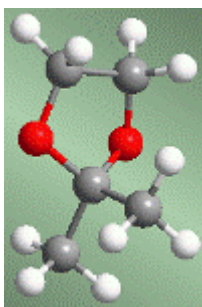
### Bamford Stevens (Reacción)

Tosilhidrazonas [2] de aldehídos o cetonas alifáticos [1] reaccionan con bases fuertes para dar alquenos [3].



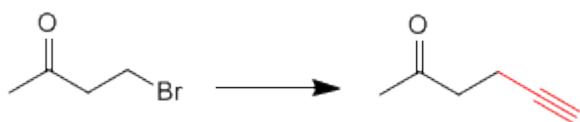


## Acetales como grupos protectores

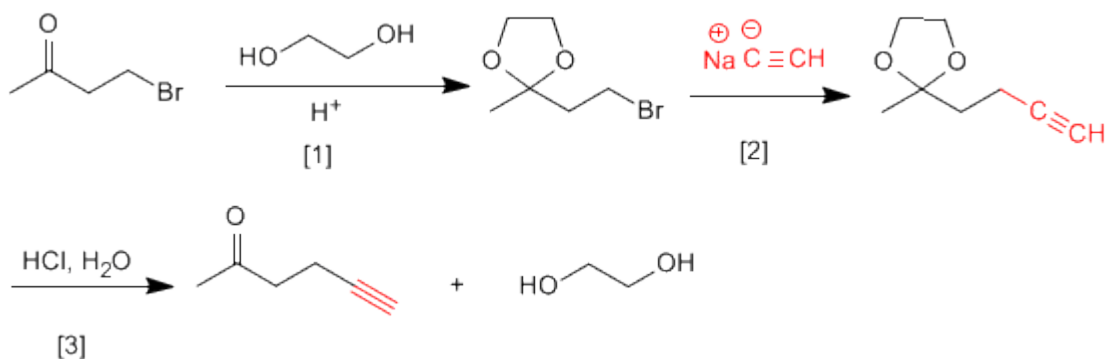


Los acetales pueden emplearse, por su estabilidad, como grupos protectores del carbonilo. El acetal es un éter, muy estable en medios básicos, aunque rompe en presencia de medios ácidos. En muchos procesos de síntesis el grupo carbonilo es incompatible con el reactivo utilizado. En estos casos debe protegerse para evitar que reaccione. La inestabilidad del acetal en medio ácido puede emplearse para desproteger el carbonilo.

Veamos algunos ejemplos:



Esta transformación requiere una sustitución, empleando como nucleófilo un acetiluro de sodio. El nucleófilo puede atacar también al grupo carbonilo, para evitarlo vamos a protegerlo.

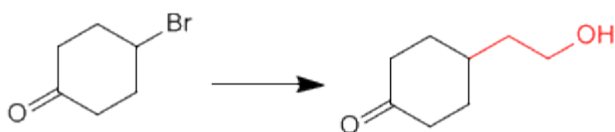


[1] Protección de la cetona.

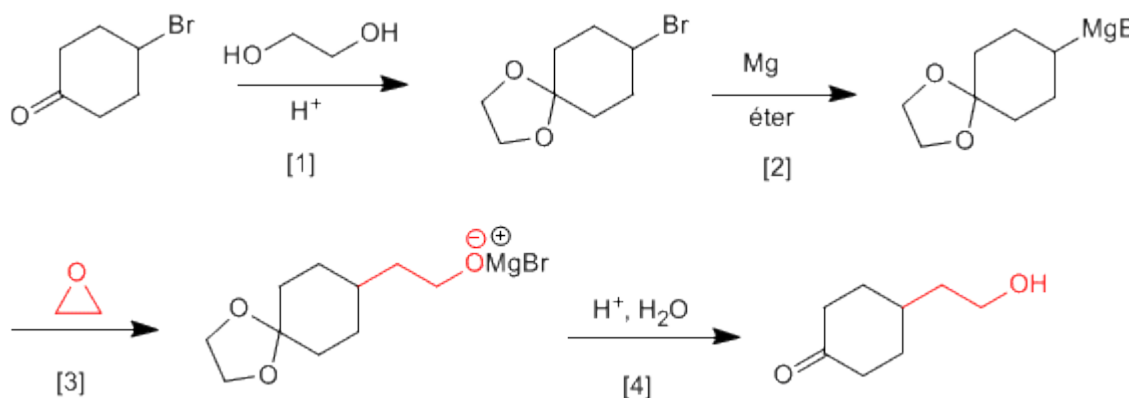
[2] Ataque del acetiluro al carbono del bromo.

[3] Desprotección del carbonilo

Veamos un segundo ejemplo:



Es necesario proteger la cetona antes de formar el organometálico para evitar la dimerización del compuesto.



- [1] Protección de la cetona.  
 [2] Formación del magnesiano.  
 [3] Apertura del oxaciclopropano.  
 [4] Desprotección y protonación del alcóxido.

### Otto Paul Hermann Diels (1876 - 1954)



**Origen:** Químico alemán.

**Lugar de nacimiento:** Königshütte (hoy Chorzów, Polonia).

**Formación:** estudió química en la Universidad de Berlín entre 1895 y 1899, consiguiendo el doctorado este año.

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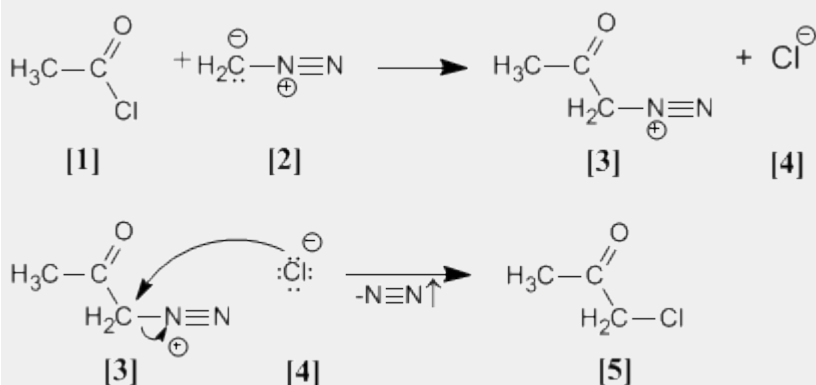
**Investigación:** En 1906 descubrió el anhídrido malónico.

Investigó en reacciones de deshidrogenación con selenio. Síntesis de  $\alpha$ -dicetonas. Pero su trabajo más importante es la reacción de Diels - Alder.

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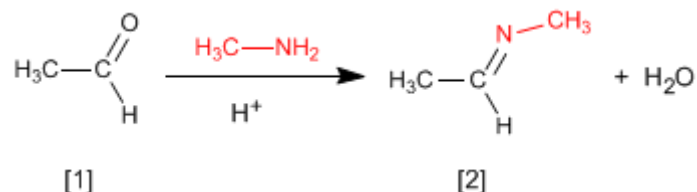
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Cloruro de acetilo **[1]** se trata con diazometano **[2]** rindiendo la sal de diazonio **[3]**. El cloruro **[4]** producido reacciona con la sal de diazonio para dar la  $\alpha$ -clorocetona **[5]**.



## Formación de Iminas

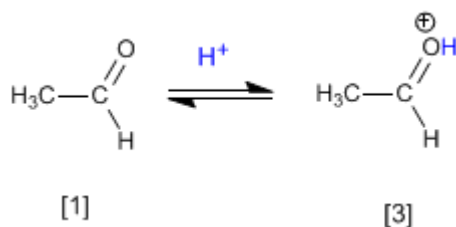
La reacción de aldehídos o cetonas **[1]** con aminas primarias genera iminas **[2]**. La reacción se favorece en un medio ligeramente ácido (pH=4.5).



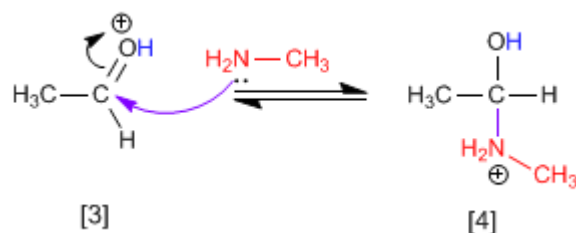
El control del pH es fundamental, puesto que se requiere la protonación del oxígeno del carbonilo para favorecer el ataque nucleófilo.

### Mecanismo:

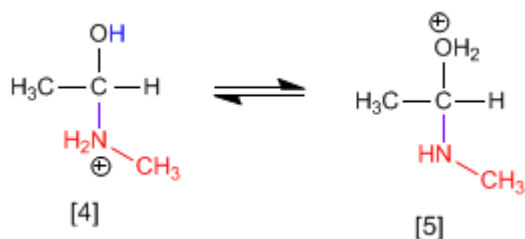
**Etapla 1.** Protonación del grupo carbonilo que aumenta la polaridad positiva sobre el carbono y favorece el ataque nucleófilo.



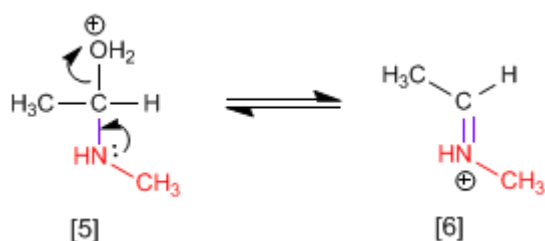
**Etapla 2.** Ataque nucleófilo de la amina primaria al carbono carbonilo.



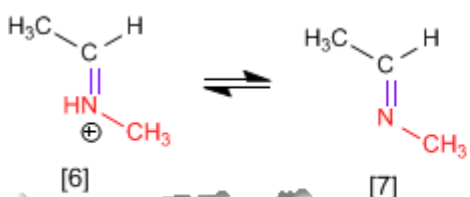
**Etapla 3.** Protonación del grupo hidroxilo para transformarlo en buen grupo saliente.



**Etapla 4.** Pérdida de agua y formación de la imina protonada.



### Etapa 5. Desprotonación del catión.



### George A. Olah (1927 - )



**Origen:** Químico estadounidense.

**Lugar de nacimiento:** Budapest

**Formación:** Se doctoró en la Universidad de Budapest en 1949

**Docencia:** Trabajó en el departamento de química orgánica de la Academia de Ciencias de Hungría y posteriormente en la Universidad de Cleveland.

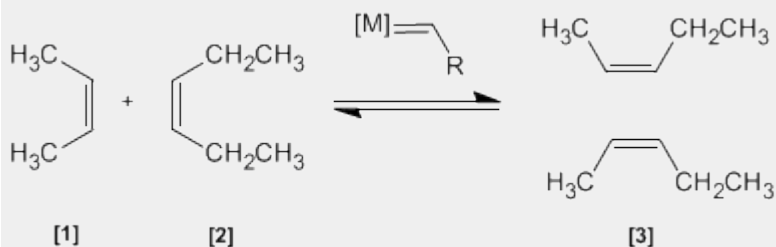
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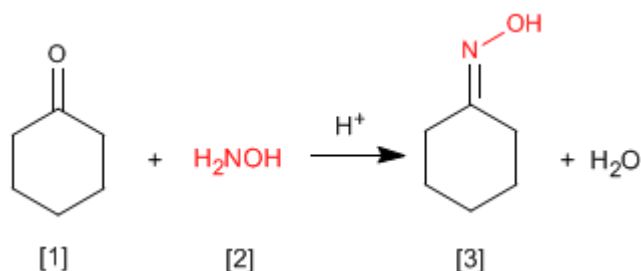
### Metátesis de Alquenos

En esta reacción dos alquenos **[1]** y **[2]** son tratados con un metal de transición que actúa como catalizador, dando una mezcla de alquenos **[3]** (incluyendo isómeros Z/E). Este productos se obtiene por intercambio de grupos alquilideno.

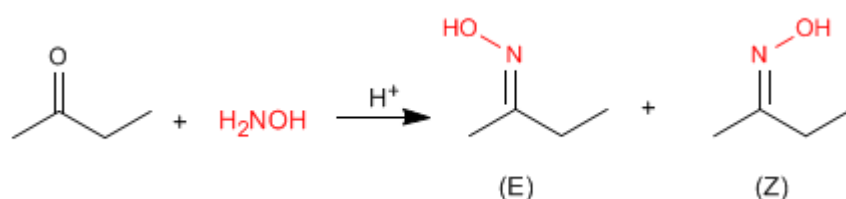


## Formación de Oximas

Las oximas [3] se obtienen por reacción de aldehídos o cetonas [1] e hidroxilamina [2] en un medio débilmente ácido. El mecanismo es análogo al de formación de iminas.



Las oximas de aldehídos y cetona asimétricas presentan isomería Z/E dependiendo de la posición del hidroxilo.



Las iminas e hidrazonas (que comentaremos a continuación) también presentan esta característica.

### George A. Olah (1927 - )



**Origen:** Químico estadounidense.

**Lugar de nacimiento:** Budapest

**Formación:** Se doctoró en la Universidad de Budapest en 1949

**Docencia:** Trabajó en el departamento de química orgánica de la Academia de Ciencias de Hungría y posteriormente en la Universidad de Cleveland.

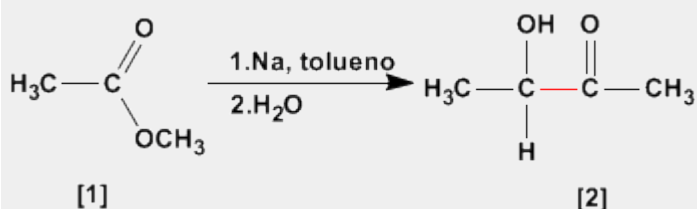
**Industria:** Trabajó en los laboratorios de la Dow Chemical de Ontario

**Investigación:** Olah consiguió preparar carbocationes estables utilizando componentes extremadamente ácidos.

**Premio Nobel:** En 1994 obtuvo el premio Nobel de Química por sus investigaciones sobre los carbocationes

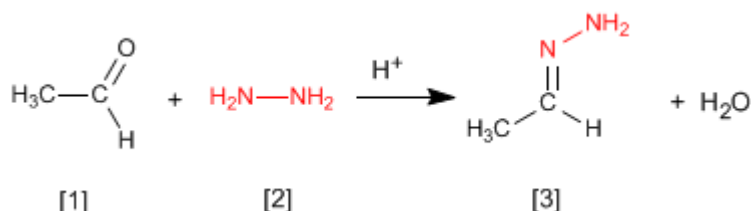
## Aciloinica (Condensación)

La condensación aciloinica transforma ésteres [1] en alfa-hidroxicetonas [2]. Esta reacción se realiza con sodio metal en disolvente inerte.

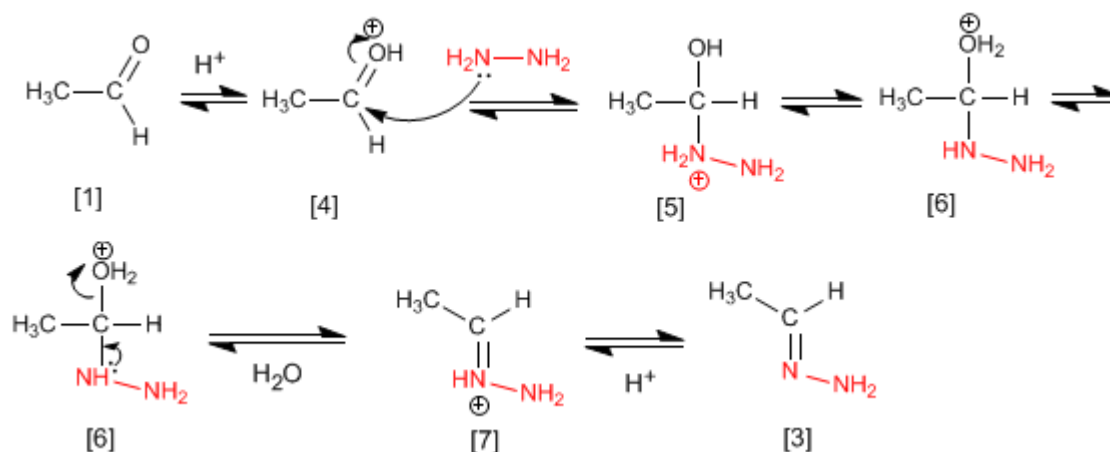


## Formación de Hidrazonas

Las hidrazonas [3] se obtienen por reacción de aldehídos o cetonas [1] con hidrazina [2]. Igual que en el caso de las iminas y oximas requiere pH=4.



Aunque el mecanismo es análogo al de formación de iminas, comentaremos de nuevo los pasos.



El etanal [1] se protona formando su ácido conjugado [4]. La importante polaridad del carbono carbonilo de [4] favorece el ataque de la hidrazina [2] para formando el intermedio [5]. El compuesto [5] intercambia un protón entre el nitrógeno y el oxígeno, transformando el grupo hidroxilo en agua (buen grupo saliente). El intermedio [6] pierde una molécula de agua transformándose en [7], cuya desprotonación da la hidrazona final [3].

### Kurt Alder (1902 - 1958)



**Origen:** Químico alemán.

**Lugar de nacimiento:** Königshütte (hoy Chorzów, Polonia).

**Formación:** estudió en la Universidad de Kiel. Bajo la supervisión del químico alemán Otto Diels, su jefe e instructor en Kiel.

**Docencia:** Alder ejerció como profesor de química en las universidades de Kiel y Colonia.

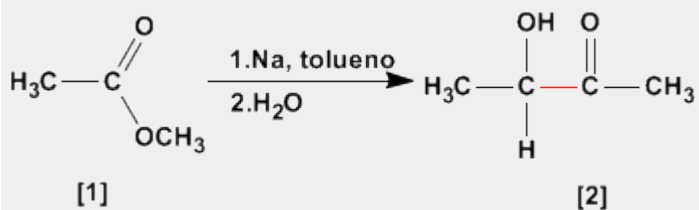
**Investigación:** Alder se especializó en la síntesis diénica (conocida más tarde como la reacción Diels - Alder) que consiste fundamentalmente en el análisis y formación de compuestos orgánicos complejos.

Ya en 1928 ambos fueron coautores de un ensayo sobre este proceso.

**Premio Nobel:** En 1950 recibió el Premio Nobel junto a Diels

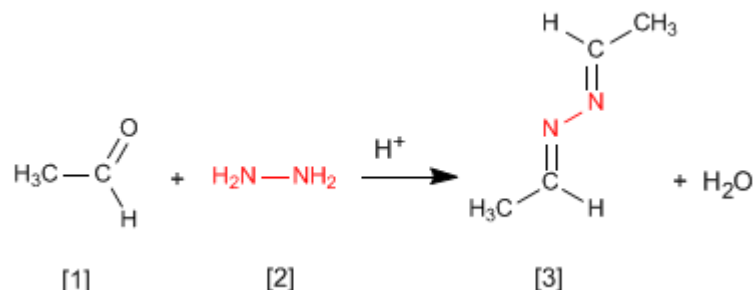
### Aciloínica (Condensación)

La condensación aciloínica transforma esteres [1] en alfa-hidroxicetonas [2]. Esta reacción se realiza con sodio metal en disolvente inerte.



## Formación de Azinas

La hidrazina [2] reacciona con dos moléculas de aldehído [1] para formar azinas [3].



El mecanismo es análogo al de formación de iminas, oximas e hidrazonas.

### George A. Olah (1927 - )



**Origen:** Químico estadounidense.

**Lugar de nacimiento:** Budapest

**Formación:** Se doctoró en la Universidad de Budapest en 1949

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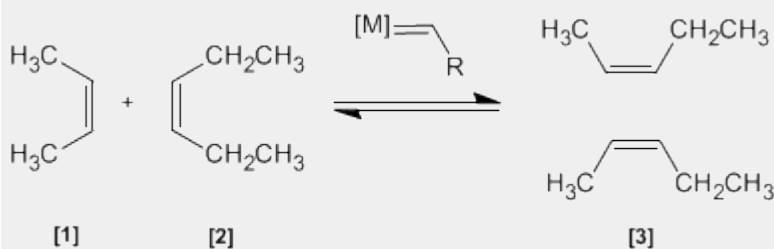
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## Metátesis de Alquenos

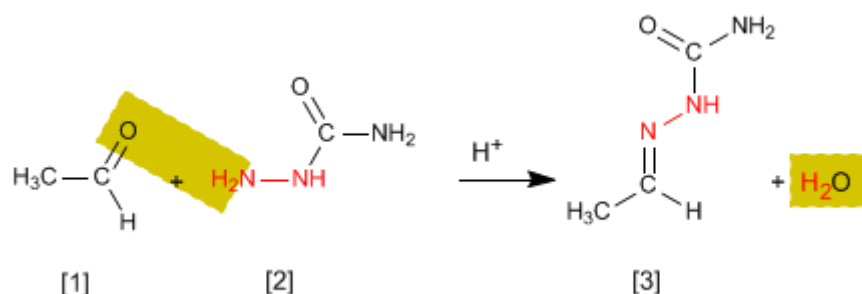
En esta reacción dos alquenos [1] y [2] son tratados con un metal de transición que actúa como catalizador, dando una mezcla de alquenos [3] (incluyendo isómeros Z/E). Este producto se obtiene por intercambio de grupos alquilideno.





## Formación de Semicarbazonas

Las semicarbazonas [3] se obtienen por reacción de aldehídos o cetonas [1] con semicarbazida [2]. Veamos un ejemplo:



El mecanismo es análogo al de formación de iminas, oximas e hidrazonas.

### Charles Friedel (1832 - 1899)



**Origen:** Químico frances..

**Lugar de nacimiento:** Estrasburgo.

**Formación:** estudió química en la Universidad de Berlín entre 1895 y 1899, consiguiendo el doctorado este año.

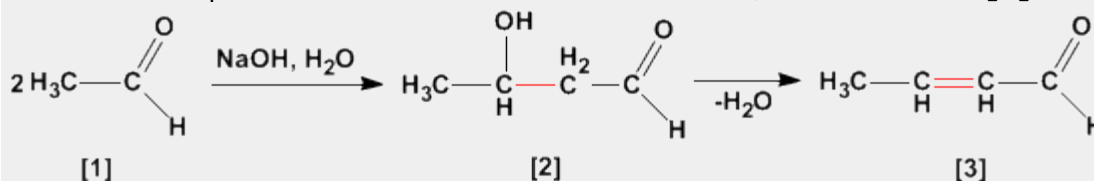
**Docencia:** Profesor en la Universidad de la Sorbona.

**Investigación:** Obtuvo el alcohol propílico. En 1877, Friedel y Crafts describieron por primera vez la reacción del benceno con un haloalcano en presencia de un ácido de Lewis. Esta reacción produce la alquilación del benceno y se conoce como alquilación de Friedl-Crafts.

**Premio Nobel:**

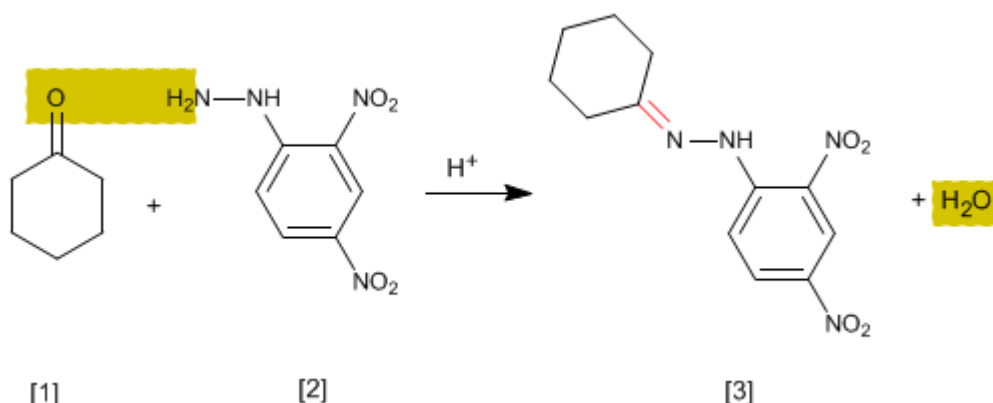
### Aldólica (Condensación)

La condensación aldólica es una reacción de aldehídos o cetonas [1] que forma 3-hidroxicarbonilos (aldoles) [2]. El 3-hidroxialdehído [2] bajo condiciones de deshidratación por calentamiento rinde un aldehído alfa,beta-insaturado [3].



## Ensayo de la 2,4-Dinitrofenilhidrazina

Se trata de un ensayo analítico específico de aldehídos y cetonas. Los carbonilos **[1]** reaccionan con 2,4-Dinitrofenilhidrazina **[2]** formando fenilhidrazonas **[3]** que precipitan de color amarillo. La aparición de precipitado es un indicador de la presencia de carbonilos en el medio.



El mecanismo de la reacción es análogo al de formación de iminas.

### Kurt Alder (1902 - 1958)



**Origen:** Químico alemán.

**Lugar de nacimiento:** Königshütte (hoy Chorzów, Polonia).

**Formación:** estudió en la Universidad de Kiel. Bajo la supervisión del químico alemán Otto Diels, su jefe e instructor en Kiel.

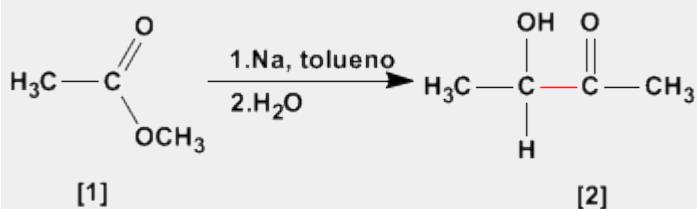
**Docencia:** Alder ejerció como profesor de química en las universidades de Kiel y Colonia.

**Investigación:** Alder se especializó en la síntesis diénica (conocida más tarde como la reacción Diels - Alder) que consiste fundamentalmente en el análisis y formación de compuestos orgánicos complejos. Ya en 1928 ambos fueron coautores de un ensayo sobre este proceso.

**Premio Nobel:** En 1950 recibió el Premio Nobel junto a Diels

### Aciloinica (Condensación)

La condensación aciloinica transforma esteres **[1]** en alfa-hidroxicetonas **[2]**. Esta reacción se realiza con sodio metal en disolvente inerte.



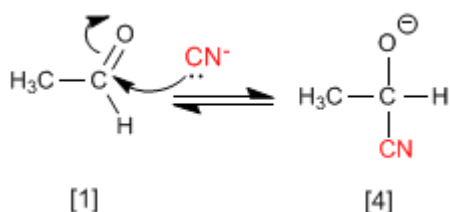
## Formación de Cianhidrinas

Las cianhidrinas **[3]** se forman por reacción de aldehídos o cetonas **[1]** con ácido cianhídrico **[2]** y son compuestos que contienen un grupo ciano y un hidroxilo sobre el mismo carbono.

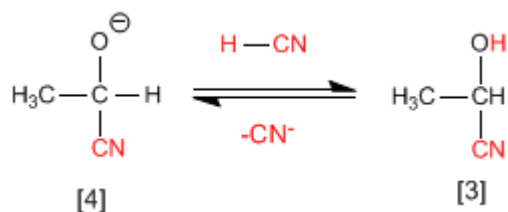


El mecanismo de la reacción transcurre en dos etapas:

**Etapla 1.** Los iones cianuro actúan como nucleófilos atacando al carbono carbonilo. El ácido cianhídrico es demasiado débil para generar cantidades importantes de cianuro, por ello, se añade cianuro de sodio o potasio al medio, garantizando la cantidad suficiente de cianuro para que la reacción transcurra en buen rendimiento.



**Etapla 2.** En este paso el ión alcóxido **[4]** se protona arrancando hidrógenos al ácido cianhídrico. En esta etapa se regeneran los iones cianuro.



### Kurt Alder (1902 - 1958)



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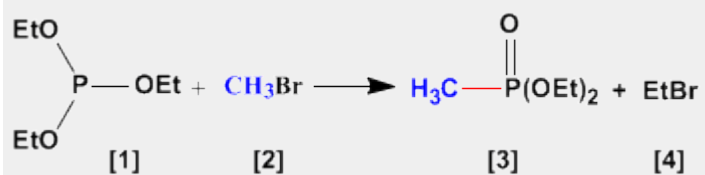
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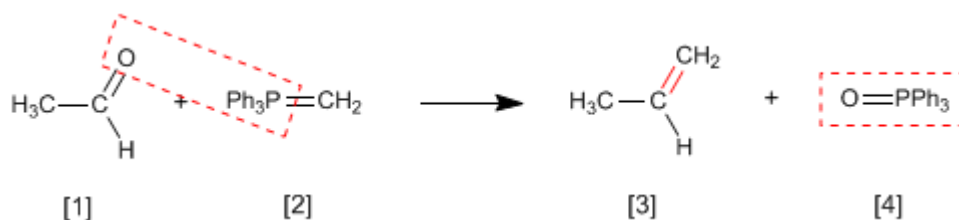
### Arbuzov (Reacción)

La reacción de Arbuzov se emplea en la síntesis de fosfonatos **[3]** a partir de fosfitos **[1]**. Los fosfonatos obtenidos en la síntesis de Arbuzov se emplean como materiales de partida en la síntesis de Horner-Wittig.



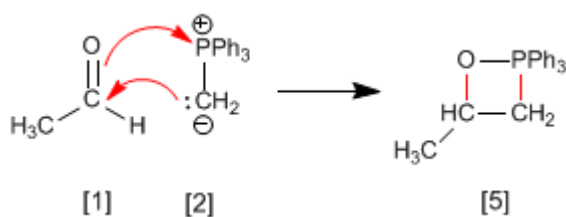
## Reacción de Wittig

La reacción de Wittig emplea iluros de fósforo [2] para transformar aldehídos y cetonas [1] en alquenos [3]. Como subproducto se obtiene el óxido de trifenilfosfina [4].

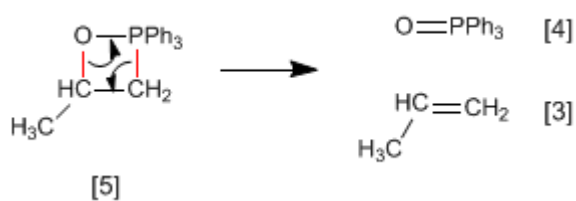


En el mecanismo de la reacción el iluro y el carbonilo se combinan para formar un oxafosfetano que rompe dejando libre el alqueno final.

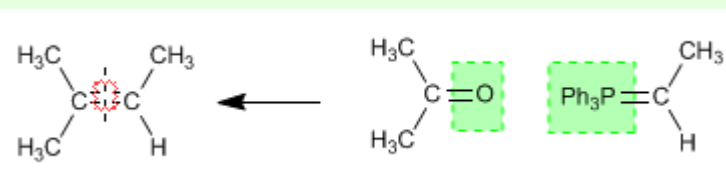
**Etapas 1.** El etanal y el iluro se combinan formando el fosfetano.



**Etapas 2.** El fosfetano rompe formando el alqueno y óxido de trifenilfosfina.

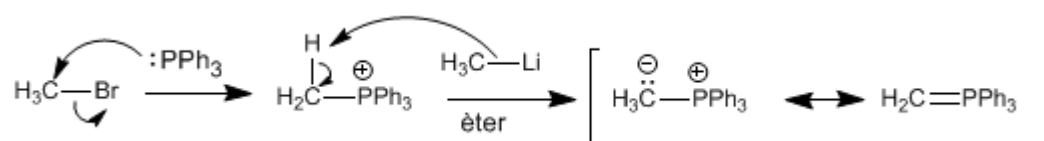


Ejemplo - Obtener mediante Wittig el 2-Metilbut-2-eno



Se rompe el alqueno por el doble enlace y a cada carbono se le agrega el grupo encerrado en verde.

Los **iluros de fósforo** se preparan mediante reacción de haloalcanos y trifenilfosfina, seguido de desprotonación del carbono con base fuerte (organometálicos de litio).



### Charles Friedel (1832 - 1899)



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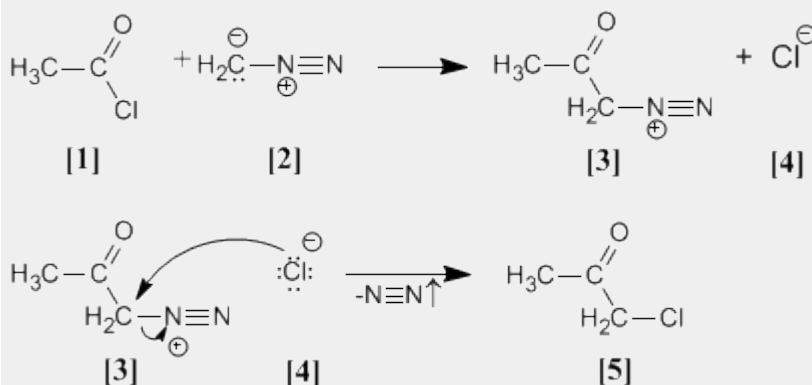
**Docencia:** Profesor en la Universidad de la Sorbona.

**Investigación:** Obtuvo el alcohol propílico. En 1877, Friedel y Crafts describieron por primera vez la reacción del benceno con un haloalcano en presencia de un ácido de Lewis. Esta reacción produce la alquilación del benceno y se conoce como alquilación de Friedl-Crafts.

**Premio Nobel:**

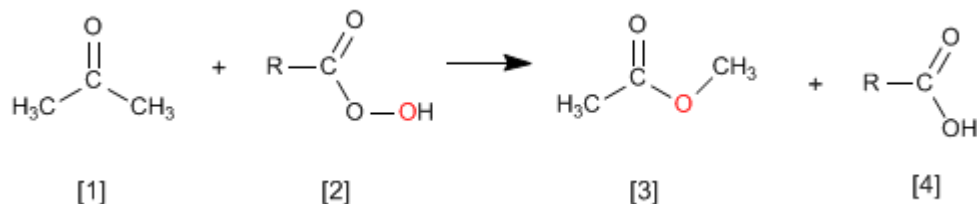
### Arndt Eistert (Síntesis)

Cloruro de acetilo **[1]** se trata con diazometano **[2]** rindiendo la sal de diazonio **[3]**. El cloruro **[4]** producido reacciona con la sal de diazonio para dar la  $\alpha$ -clorocetona **[5]**.

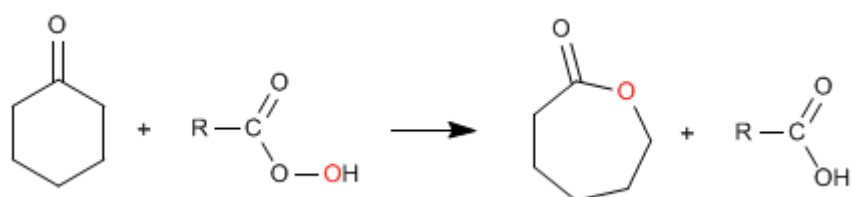


## Oxidación de Baeyer Villiger

La reacción de cetonas **[1]** con perácidos **[2]** produce ésteres **[3]**. El oxígeno del perácido se inserta entre el carbono carbonilo y el carbono alfa de la cetona. Esta reacción fue descrita por Adolf von Baeyer y Victor Villiger in 1899.

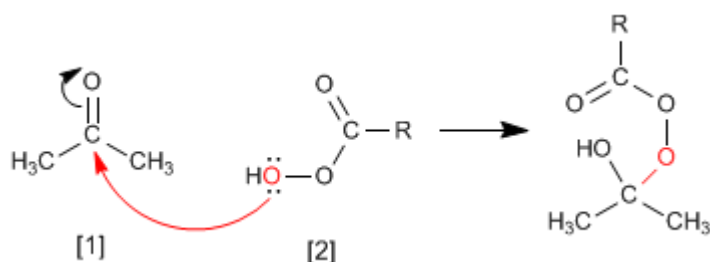


A partir de cetonas cíclicas se obtienen ésteres cíclicos (lactonas)

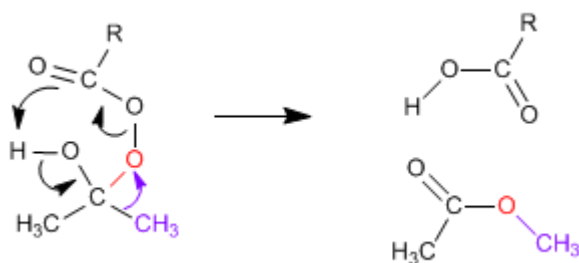


El mecanismo de Baeyer Villiger comienza con el ataque nucleófilo del perácido sobre el carbonilo, seguido de la migración del sustituyente desde el grupo carbonilo al oxígeno del perácido.

**Etapas 1.** Adición del perácido al carbonilo

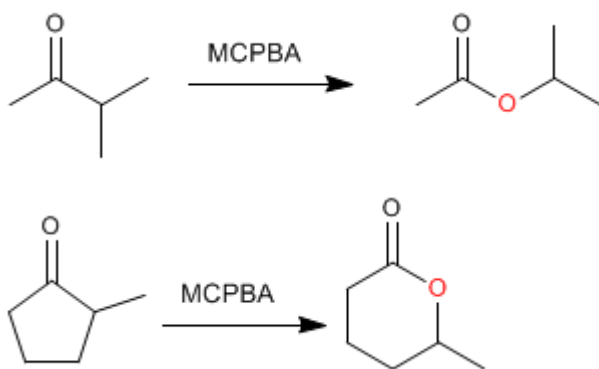


**Etapas 2.** Migración del sustituyente desde carbono carbonilo hacia el oxígeno (rojo)

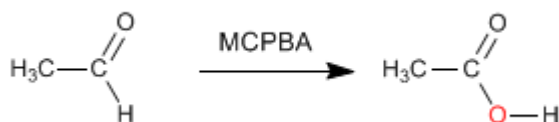


Cuando la cetona tiene dos sustituyentes diferentes migra mejor el más sustituido. Existe un orden de migración que nos ayuda a decidir que sustituyente pasa a unirse al oxígeno del perácido.

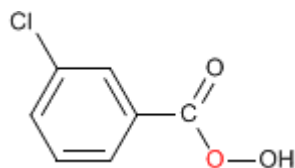
Orden de migración: H > carbono terciario > ciclohexilo > carbono secundario » fenilo > carbono primario > metilo



Como puede observarse en el orden de migración, el grupo que mejor migra, por su pequeño tamaño, es el hidrógeno, por ello, al tratar aldehídos con perácidos se produce la migración del hidrógeno formándose ácidos carboxílicos.



El **MCPBA** (Ácido meta-cloroperoxibenzoico) es un perácido ampliamente utilizado en la epoxidación de alquenos y también en Baeyer-Villiger. La fórmula del MCPBA se muestra a continuación.



#### Charles Friedel (1832 - 1899)



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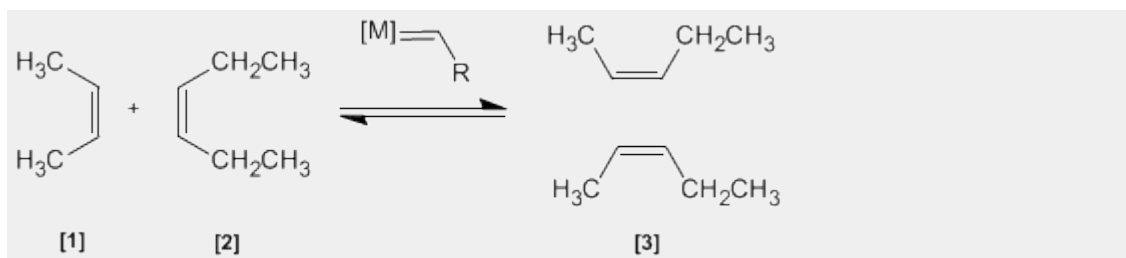
**Investigación:** Obtuvo el alcohol propílico. En 1877, Friedel y Crafts describieron por primera vez la reacción del benceno con un haloalcano en presencia de un ácido de Lewis. Esta reacción produce la alquilación del benceno y se conoce como alquilación de Friedl-Crafts.

**Premio Nobel:**

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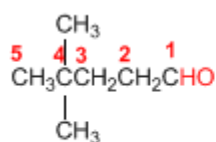




## Nomenclatura de Aldehídos y Cetonas - Reglas IUPAC

**Regla 1.** Los aldehídos se nombran reemplazando la terminación **-ano** del alcano correspondiente por **-al**. No es necesario especificar la posición del grupo aldehído, puesto que ocupa el extremo de la cadena (localizador 1).

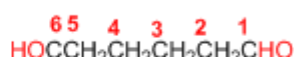
Cuando la cadena contiene dos funciones aldehído se emplea el sufijo **-dial**.



4,4-Dimetilpentanal

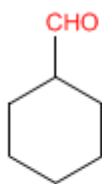


Hex-4-enal

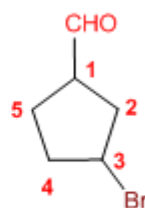


Hexanodial

**Regla 2.** El grupo **-CHO** se denomina **-carbaldehído**. Este tipo de nomenclatura es muy útil cuando el grupo aldehído va unido a un ciclo. La numeración del ciclo se realiza dando localizador 1 al carbono del ciclo que contiene el grupo aldehído.

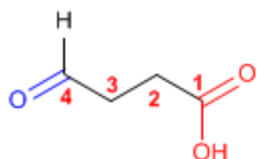


Ciclohexanocarbaldehído

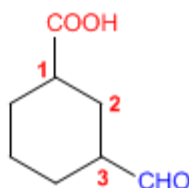


3-Bromociclopentanocarbaldehído

**Regla 3.** Cuando en la molécula existe un grupo prioritario al aldehído, este pasa a ser un sustituyente que se nombra como oxo- o formil-.



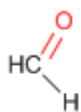
Ácido 4-oxobutanoico



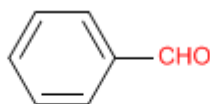
Ácido 3-formilciclohexanocarboxílico

Tanto **-carbaldehído** como **formil-** son nomenclaturas que incluyen el carbono del grupo carbonilo. **-carbaldehído** se emplea cuando el aldehído es grupo funcional, mientras que **formil-** se usa cuando actúa de sustituyente.

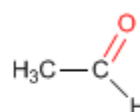
**Regla 4.** Algunos nombres comunes de aldehídos aceptados por la IUPAC son:



Formaldehído  
(Metanal)

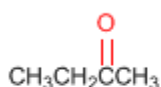


Benzaldehído  
(Benceno**carbaldehído**)

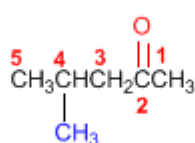


Acetaldehído  
(Etanal)

**Regla 5.** Las cetonas se nombran sustituyendo la terminación **-ano** del alcano con igual longitud de cadena por **-ona**. Se toma como cadena principal la de mayor longitud que contiene el grupo carbonilo y se numera para que éste tome el localizador más bajo.



Butan**ona**

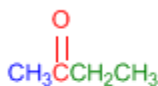


4-Metil-2-pentan**ona**

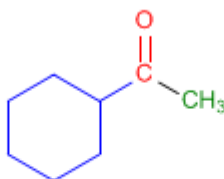


3-Metilciclohexan**ona**

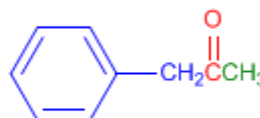
**Regla 6.** Existe un segundo tipo de nomenclatura para las cetonas, que consiste en nombrar las cadenas como sustituyentes, ordenándolas alfabéticamente y terminando el nombre con la palabra cetona.



Etil metil **cetona**

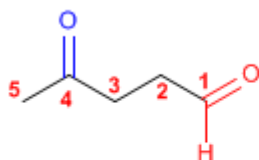


Ciclohexil metil **cetona**

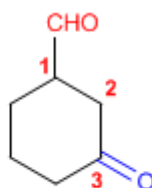


Fenil metil **cetona**

**Regla 7.** Cuando la cetona no es el grupo funcional de la molécula pasa a llamarse **OXO-**.



4-Oxopentan**al**

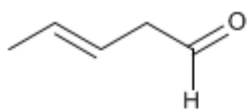


3-Oxociclohexano**carbaldehído**

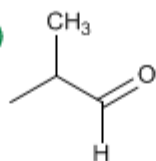
## Nomenclatura de Aldehídos y Cetonas - Problema 9.1

Nombra los siguientes aldehídos y cetonas:

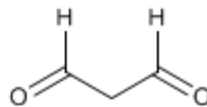
a)



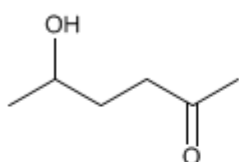
b)



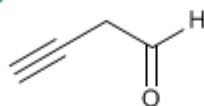
c)



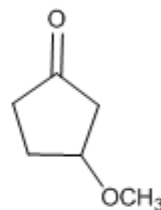
d)



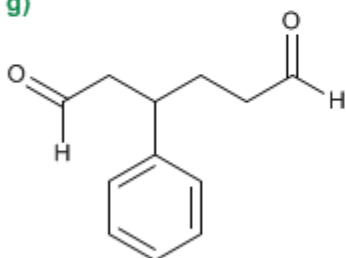
e)



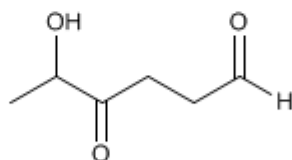
f)



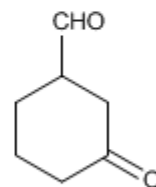
g)



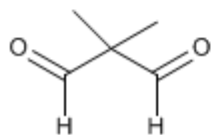
h)



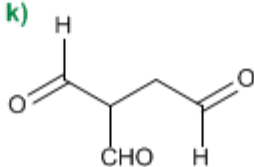
i)



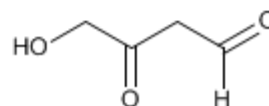
j)



k)

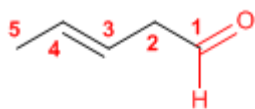


l)

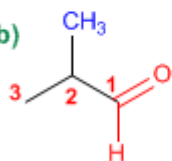


Solución

a)



b)



1. Cadena principal: 5 carbonos (pentano)

2. Numeración: comienza en el aldehído (grupo funcional)

Grupo funcional: aldehído

3. Nombre: Pent-3-enal

1. Cadena principal: 3 carbonos (propano)

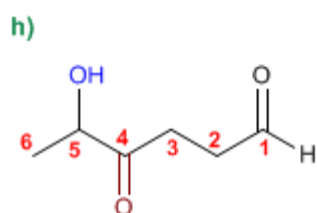
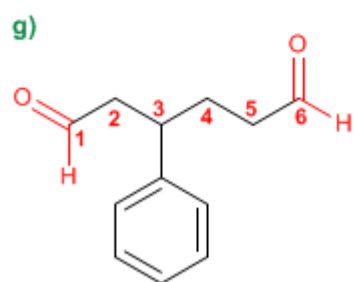
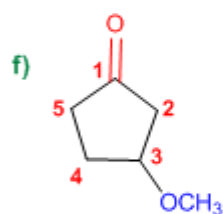
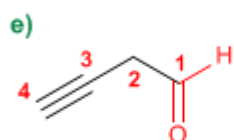
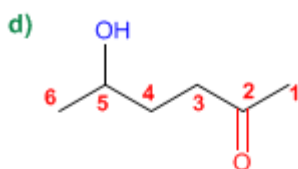
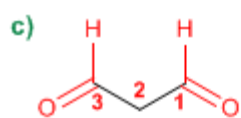
2. Numeración: localizador más bajo al aldehído.

3. Grupo funcional: aldehído

4. Sustituyentes: metilo en 2.

5. Nombre: 2-Metilpropanal

Los aldehídos y cetonas son prioritarios sobre alquenos y alquinos, y se numeran otorgándoles el localizador más bajo



1. Cadena principal: 3 carbonos (propano)
2. Grupo funcional: aldehído (dialdehído)
3. Nombre: Propanodial

1. Cadena principal: 6 carbonos (hexano)
2. Grupo funcional: cetona
3. Numeración: asignar el menor localizador a la cetona
4. Sustituyentes: hidroxí en 5.
5. Nombre: 5-Hidroxihexan-2-ona

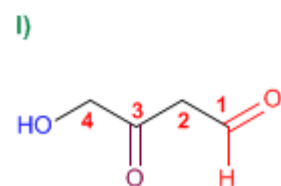
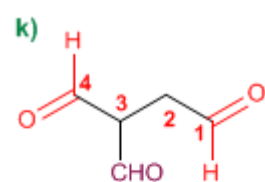
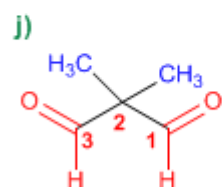
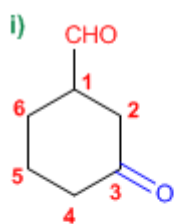
1. Cadena principal: 4 carbonos (butano)
2. Grupo funcional: aldehído
3. Numeración: asignar el menor localizador al aldehído
4. Nombre: But-3-inal

1. Cadena principal: ciclo de 5 miembros (ciclopentano)
2. Grupo funcional: cetona
3. Numeración: comienza en la cetona y prosigue hacia el sustituyente
4. Sustituyentes: metoxi en 3.
5. Nombre: 3-Metoxiciclopentanona

1. Cadena principal: 6 carbonos (hexano)
2. Grupo funcional: aldehído (dialdehído)
3. Numeración: comienza en el extremo que otorga al fenilo el localizador más bajo.
4. Sustituyentes: fenilo en 3.
5. Nombre: 3-Fenilhexanodial

1. Cadena principal: 6 carbonos (hexano)
2. Grupo funcional: aldehído
3. Numeración: asignar el menor localizador al aldehído
4. Sustituyentes: hidroxí en 5 y oxo en 4.
5. Nombre: 5-Hidroxí-4-oxohexanal

Los aldehídos son prioritarios sobre las cetonas que pasan a nombrarse como sustituyentes (oxo-)



1. Cadena principal: ciclo de 6 miembros (ciclohexano)
2. Grupo funcional: aldehído (-carbaldehído)
3. Numeración: menor localizador al grupo -CHO (este no se numera)
4. Sustituyentes: cetona (oxo-) en 3
5. Nombre: 3-Oxociclohexanocarbaldehído

1. Cadena principal: 3 carbonos (propano)
2. Grupo funcional: aldehído (dialdehído)
3. Sustituyentes: metilos en 2,2.
4. Nombre: 2,2-Dimetilpropanodial

1. Cadena principal: 4 carbonos (butano)
2. Grupo funcional: aldehído
3. Sustituyentes: formil en 3
4. Nombre: 3-Formilbutanodial

1. Cadena principal: 4 carbonos (butano)
2. Grupo funcional: aldehído
3. Numeración: asignar el menor localizador al aldehído
4. Sustituyentes: hidroxil en 4 y oxo en 3.
5. Nombre: 4-Hidroxil-3-oxobutanal



## Nomenclatura de Aldehídos y Cetonas - Problema 9.2

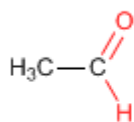
PRINT EMAIL

Dibuja la estructura de los siguientes aldehídos y cetonas:

- |   |                                  |
|---|----------------------------------|
| a) Etanal (acetaldehído)                          | g) 2,5-Dioxooctanodial           |
| b) 3-Metilbutanal                                 | h) 1,3-Ciclohexanodiona          |
| c) Benzaldehído                                   | i) 3-Metil-3-pental              |
| d) 4-Hidroxiciclohexanocarbaldehído               | j) 3-Oxobutanal                  |
| e) 3-Hidroxi-4-metil-5-oxociclohexanocarbaldehído | k) 3-Hidroxiciclopentanona       |
| f) 2-Metil-2,5-octanodiona                        | l) 4-Etoxi-5-fenil-3-oxoheptanal |

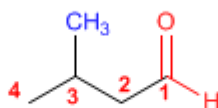
Solución

a)



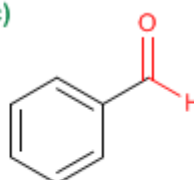
Etanal (acetaldehído)

b)

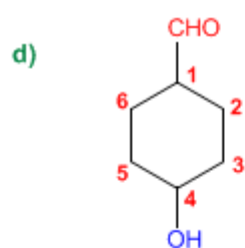


3-Metilbutanal

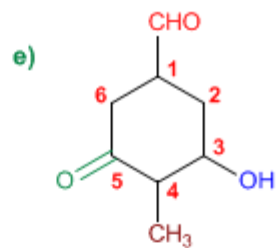
c)



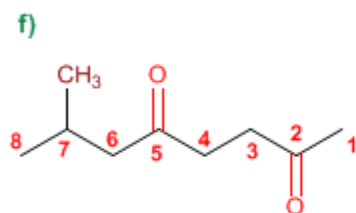
Benzaldehído



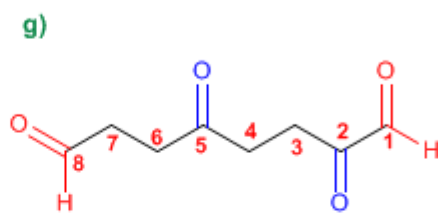
4-Hidroxiciclohexanocarbaldehído



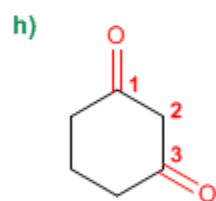
3-Hidroxi-4-metil-5-oxociclohexanocarbaldehído



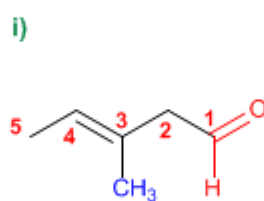
7-Metil-2,5-octanodiona



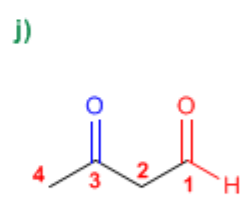
2,5-Dioxooctanodial



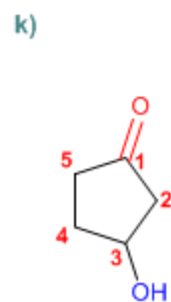
1,3-Ciclohexanodiona



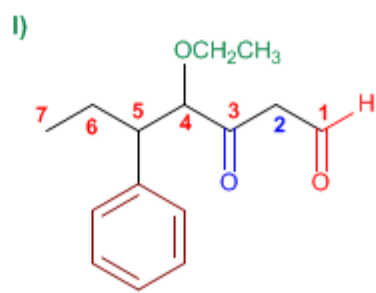
3-Metil-3-pentenal



3-Oxobutanal



3-Hidroxiciclopentanona

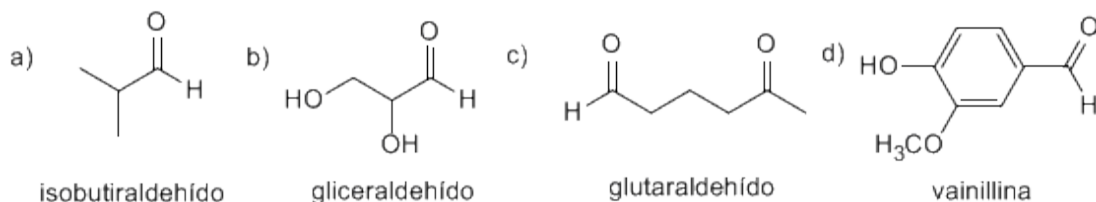


4-Etoxi-5-fenil-3-oxoheptanal

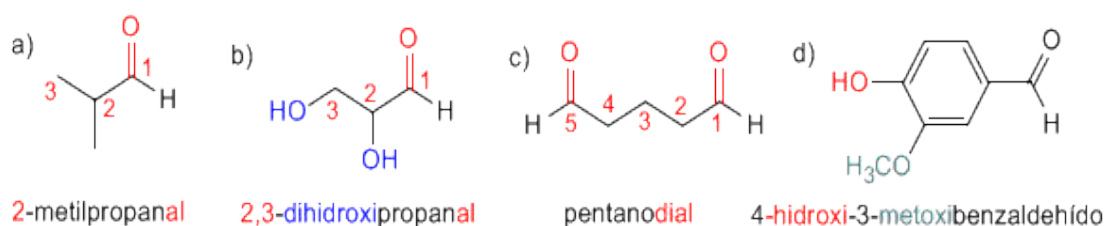
# PROBLEMAS RESUELTOS DE ALDEHÍDOS Y CETONAS

## Aldehídos y Cetonas: Problema 1

1) A continuación se dan nombres comunes y las fórmulas estructurales de algunos compuestos carbonílicos. Indique el nombre correspondiente según la IUPAC.



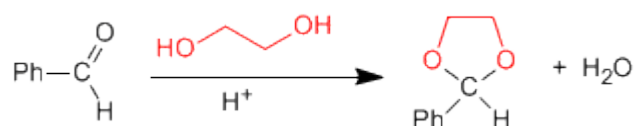
Solución



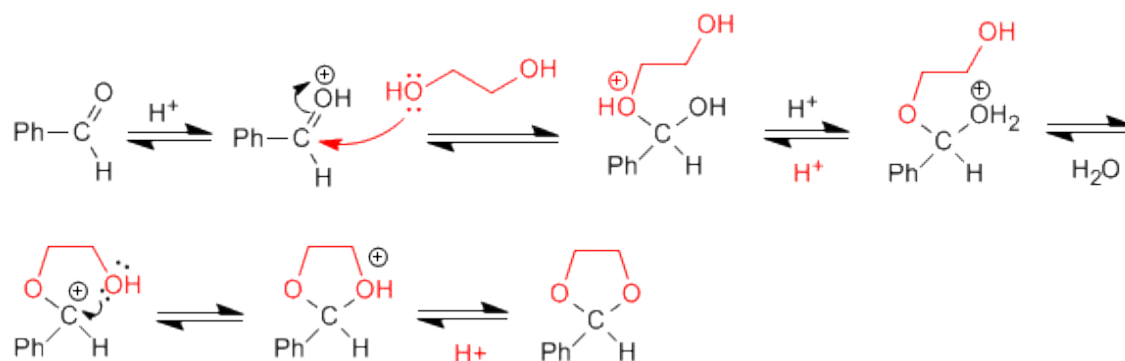
## Aldehídos y cetonas: Problema 2

Dibuje la estructura del acetal que se forma cuando el benzaldehído se calienta con 1,2-etanodiol en medio ácido. Escriba un mecanismo detallado que justifique su formación. Describa paso a paso la hidrólisis de este acetal en medio ácido acuoso.

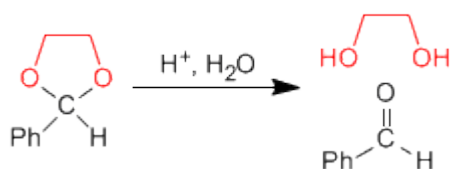
SOLUCIÓN



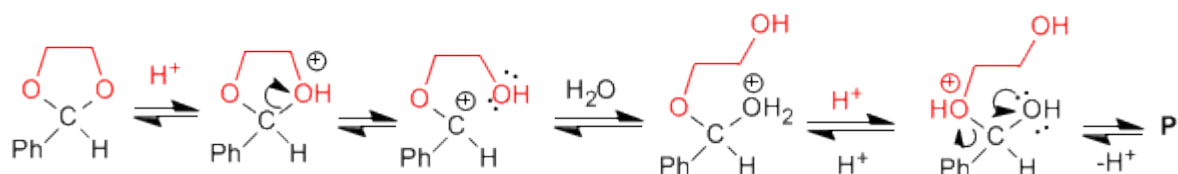
Mecanismo de formación del acetal:



La hidrólisis del acetal en medio ácido acuoso sigue es etapas inversas a la síntesis.



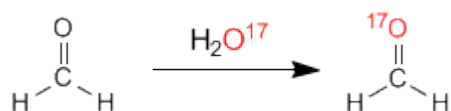
Mecanismo de hidrólisis del acetal cíclico.



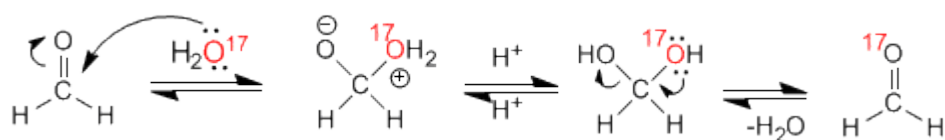
### Aldehídos y Cetonas: Problema 3

Cuando se disuelve formaldehído en agua marcada con  $^{17}\text{O}$ , se observa que después de unas horas tanto el hidrato del formaldehído como el formaldehído han incorporado el isótopo  $^{17}\text{O}$ . Sugiera una explicación razonable de este hecho.

SOLUCION



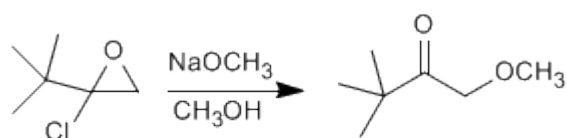
Mecanismo:



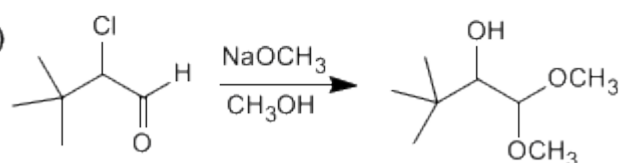
### Aldehídos y Cetonas: Problema 4

Sugiera un mecanismo razonable para una de las siguientes reacciones:

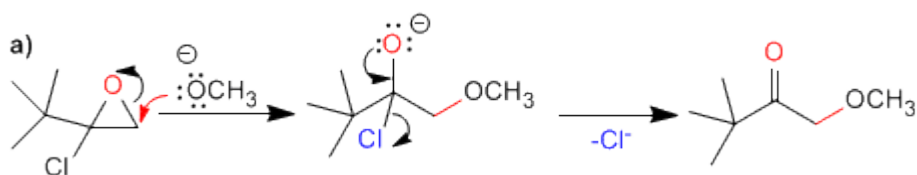
a)



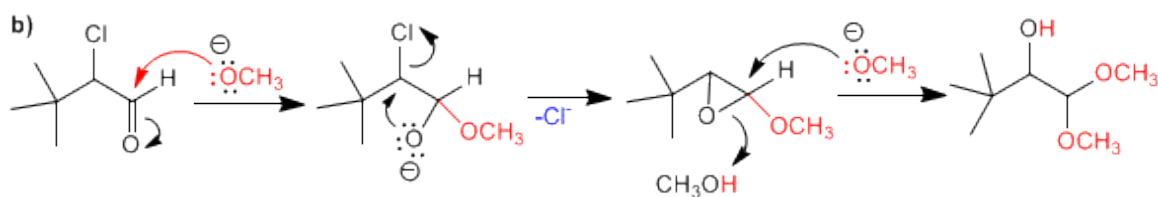
b)



## SOLUCION



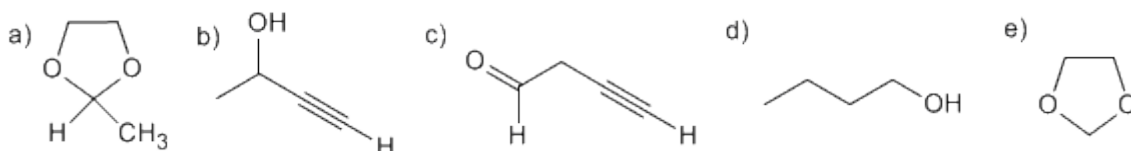
La primera etapa consiste en la apertura del oxaciclopropano sobre el carbono menos sustituido. En la segunda etapa, la cesión del par del oxígeno elimina el cloro, formándose un carbonilo.



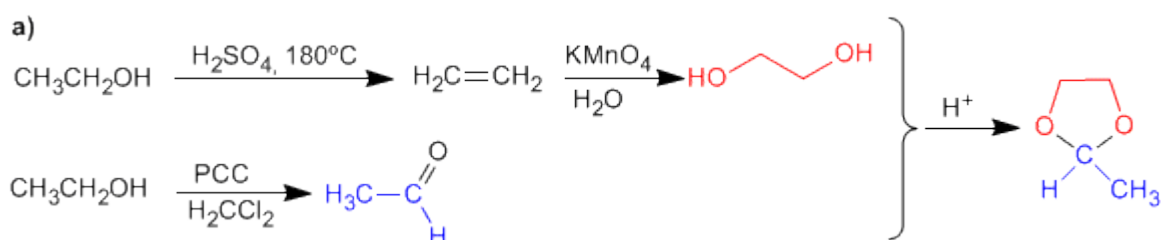
En el primer paso hay dos posibles posiciones de ataque; el carbono carbonilo y el carbono del cloro. Como el producto final no tiene metóxido en el carbono del cloro, atacamos al carbonilo. En la segunda etapa se produce una sustitución nucleófila intramolecular. Para terminar el metóxido abre el epóxido.

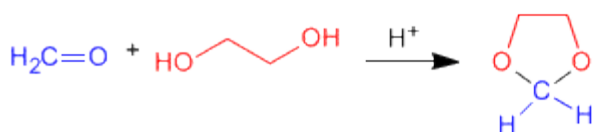
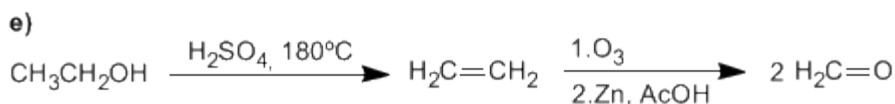
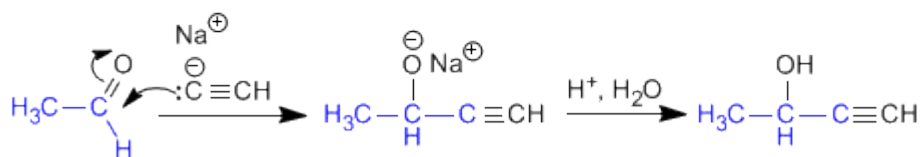
## Aldehídos y Cetonas: Problema 5

Usando etanol como fuente de todos los átomos de carbono y los reactivos que necesite, describa una síntesis eficiente de cada una de las sustancias siguientes:

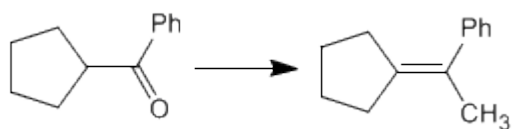


## SOLUCIÓN

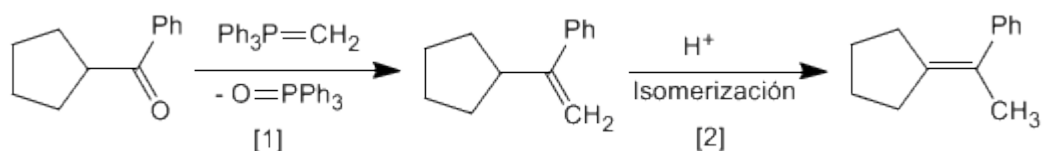




Utilizando los reactivos necesarios, indicar las etapas que permiten realizar la siguiente transformación:



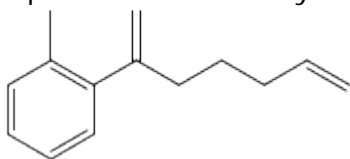
### SOLUCIÓN



[2] Isomerización en medio ácido, impulsada por la mayor estabilidad del alqueno interno.

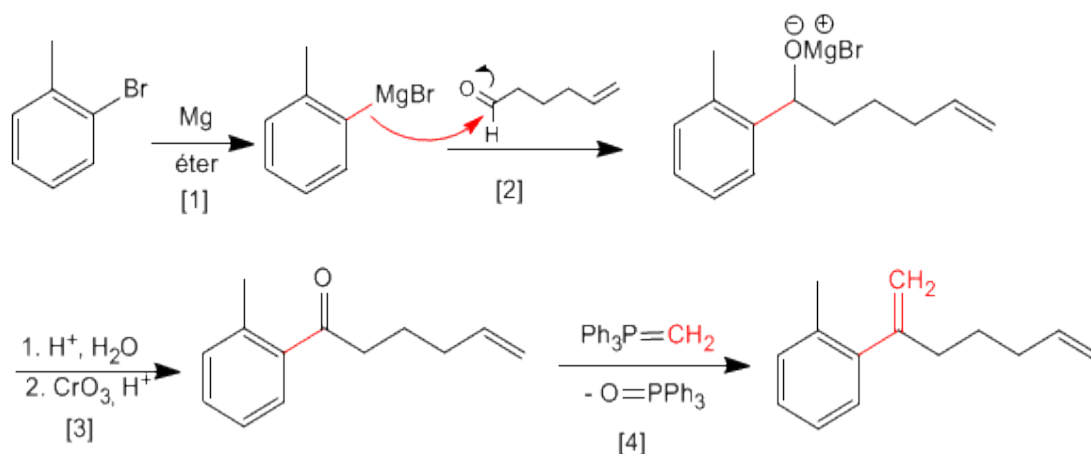
## Aldehídos y Cetonas: Problema 7

A partir de 5-hexenal y o-bromotolueno obtener el siguiente producto.



Pueden ser necesarios reactivos orgánicos e inorgánicos adicionales.

SOLUCIÓN



[1] Formación del magnesiano

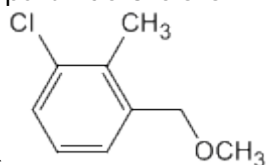
[2] Ataque nucleófilo del magnesiano al carbonilo.

[3] Hidrólisis y posterior oxidación del alcohol secundario.

[4] Reacción de Wittig entre la cetona y el trifenilmetilenfosforano.

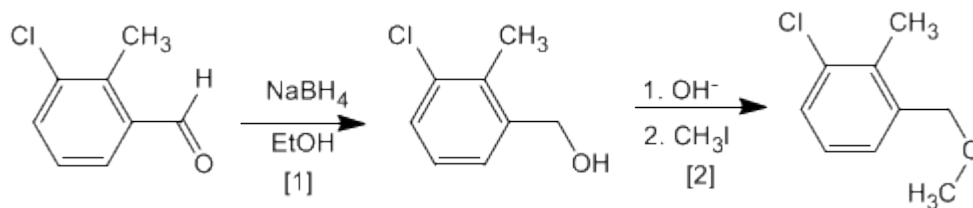
## Aldehídos y Cetonas: Problema 8

Obtener a partir de 3-cloro-2-metilbenzaldehído y de los reactivos



necesarios  
el compuesto siguiente:

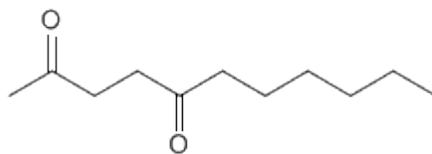
SOLUCIÓN



[1] Reducción del aldehído a alcohol

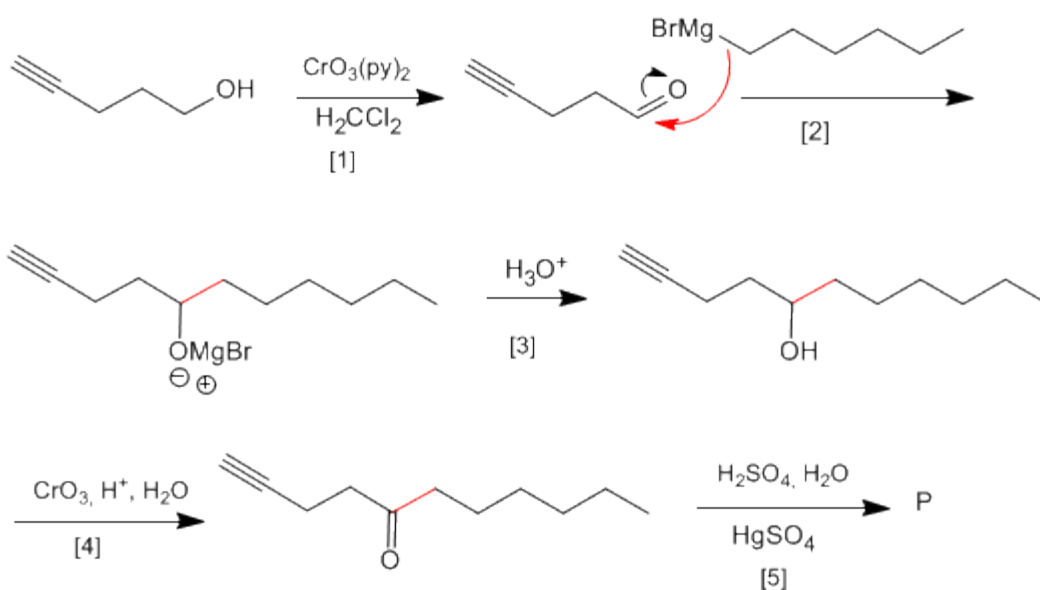
[2] Síntesis de Williamson de éteres.

## Aldehídos y Cetonas: Problema 9



A partir de 4-pentin-1-ol obtener:

SOLUCIÓN



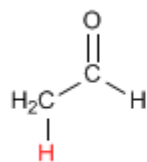
- [1] Oxidación del alcohol a aldehído
- [2] Formación del enlace carbono-carbono mediante organometálicos de magnesio
- [3] Protonación del alcohol
- [4] Oxidación del alcohol con Jones (Puedes utilizar también  $\text{CrO}_3(\text{py})_2$ )
- [5] Hidratación Markovnikov del alquino, para formar cetonas



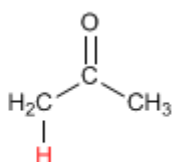
# TEORÍA DE ENOLES Y ENOLATOS

## Formación de Enolatos

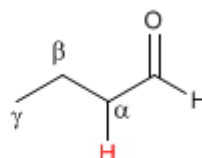
Los aldehídos y cetonas presentan hidrógenos ácidos en la posición vecina al grupo carbonilo, conocida como posición alfa. Estos hidrógenos presentan un pKa comprendido entre 18 y 21.



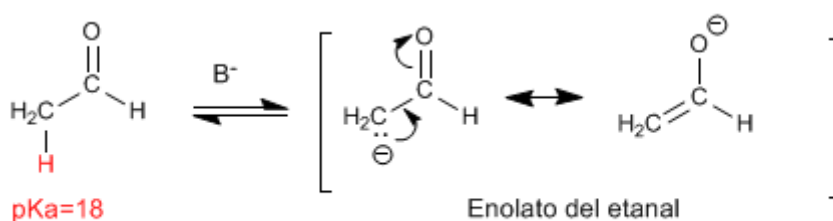
pKa=18



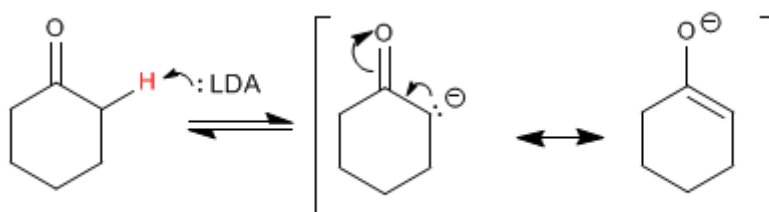
pKa=20-21



La acidez de los hidrógenos  $\alpha$  es debida a la estabilización de la base conjugada (enolato) por resonancia.



Enolato del etanal

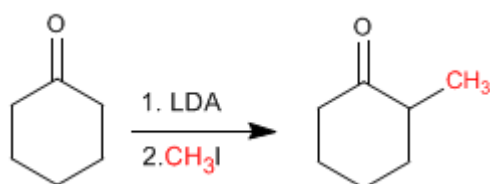


Enolato de la ciclohexanona

## Alquilación de Enolatos

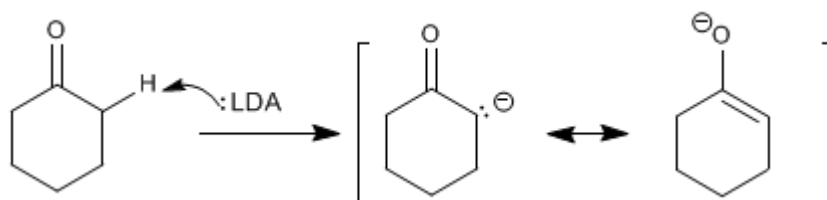
Los enolatos actúan como nucleófilos a través del carbono atacando a un gran número de electrófilos (haloalcanos, epóxidos, carbonilos, ésteres.....). En este punto nos fijaremos en la reacción entre enolatos y haloalcanos, que permite añadir cadenas carbonadas a la posición  $\alpha$  de la cadena.

La Ciclohexanona se convierte en 2-Metilciclohexanona por tratamiento con LDA seguido de yoduro de metilo.

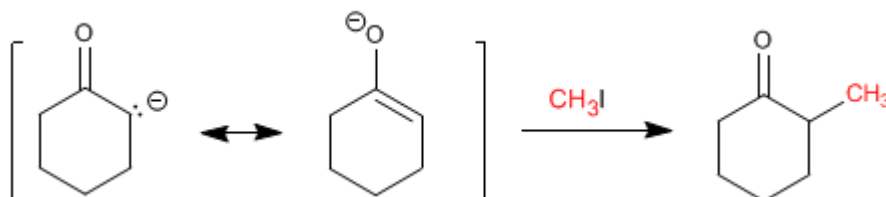


Etapas del mecanismo por el que se alquila la ciclohexanona:

### **Etapas 1.** Formación del enolato

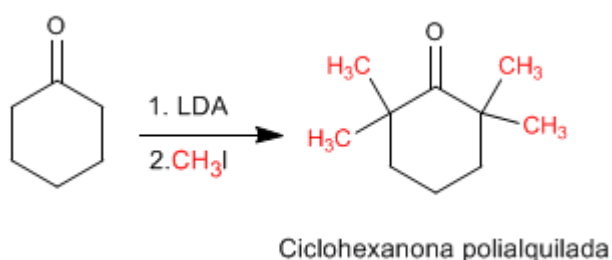


### **Etapas 2.** Ataque nucleófilo del enolato sobre el haloalcano (Reacción de tipo S<sub>N</sub>2)



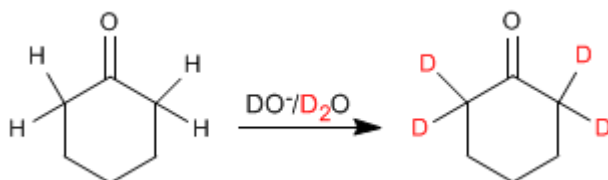
Las reacciones de alquilación tienen dos importantes problemas.

1. Competencia con la condensación aldólica. Los carbonilos en medio básico tienden a condensar para formar aldoles.
2. La reacción es difícil de controlar y tiende a polialquilar el carbonilo.



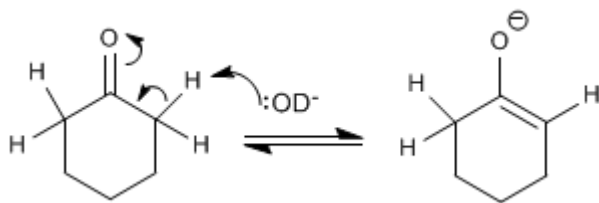
## **Intercambio hidrógeno - Deuterio**

Los aldehídos y cetonas intercambian sus hidrógenos  $\alpha$  por deuterios cuando se tratan con  $\text{DO}^-/\text{D}_2\text{O}$  o con  $\text{D}^+/\text{D}_2\text{O}$ . En medios básicos la reacción transcurre a través de enolatos y en medios ácidos los intermediarios formados son enoles.

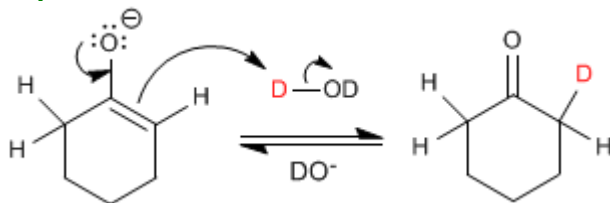


El mecanismo del intercambio hidrógeno-deuterio transcurre en los siguientes pasos:

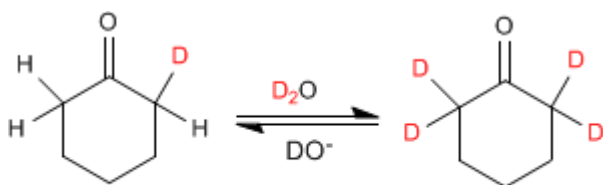
### **Etapas 1.** Formación del enolato



**Etapas 2.** Transferencia del deuterio al enolato



**Etapas 3.** Sustitución del resto de hidrógenos



## Halogenación de aldehídos y cetonas

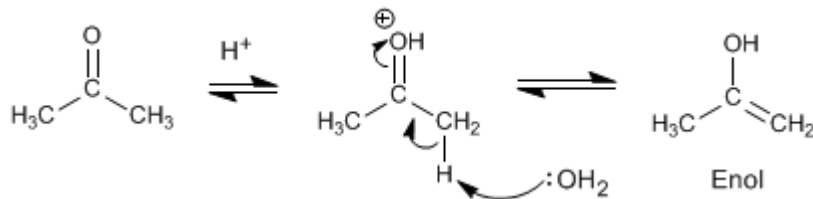
Los aldehídos y cetonas reaccionan con halógenos en medios ácidos o básicos produciéndose la sustitución de hidrógenos  $\alpha$  por halógenos.

Halogenación de la propanona en medio ácido:

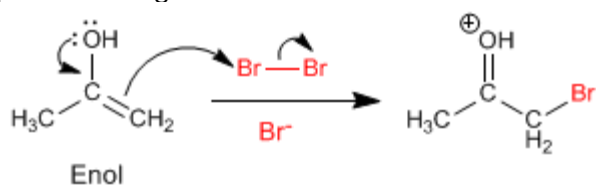


El mecanismo de halogenación en **medio ácido** tiene las siguientes etapas:

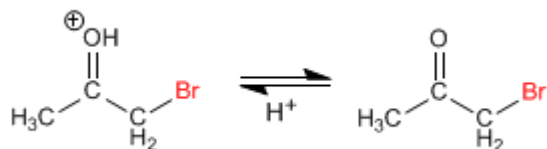
**Etapas 1.** Formación del enol



**Etapas 2.** Ataque nucleófilo del enol sobre el halógeno ayudado por la cesión del para del oxígeno.

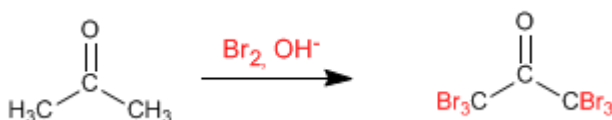


### Etapa 3. Desprotonación



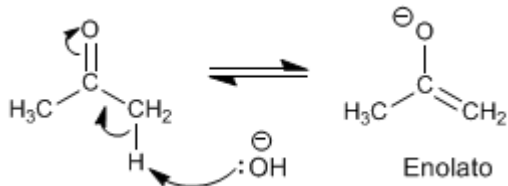
Trabajando con un equivalente de reactivo la halogenación para en una primera adición y no ocurren polihalogenaciones. El paso clave del mecanismo es la formación del enol y esta etapa requiere protonar el oxígeno del carbonilo. Una vez halogenada la posición  $\alpha$  al oxígeno se vuelve menos básico, debido al efecto electronegativo del bromo, protonándose peor.

Halogenación de la propanona en **medio básico**:

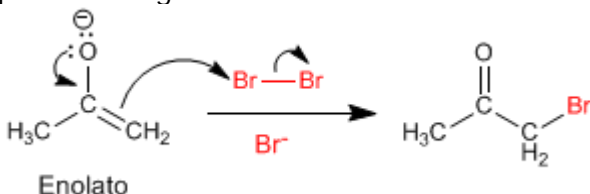


La halogenación en medio básico tiene el siguiente mecanismo:

### Etapa 1. Formación del enolato



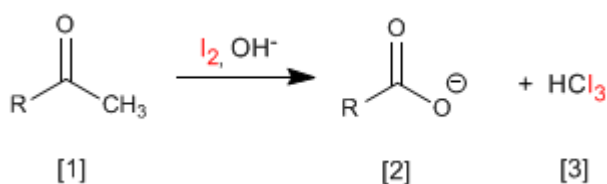
**Etapa 2.** Ataque nucleófilo del enolato sobre el halógeno ayudado por la cesión del par del oxígeno.



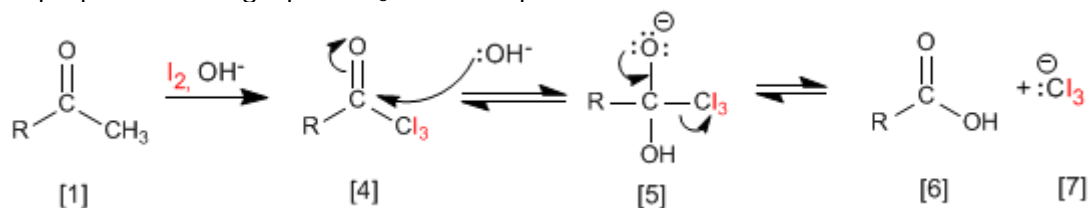
Este mecanismo se repite otras 5 veces sustituyendo todos los hidrógenos  $\alpha$  por halógenos. En este caso la reacción no para puesto que el producto halogenado es más reactivo que la propanona de partida. La base arranca mejor los hidrógenos en el producto halogenado (son más ácidos), haciendo imposible parar la reacción.

## Reacción del Haloformo (Yodoformo)

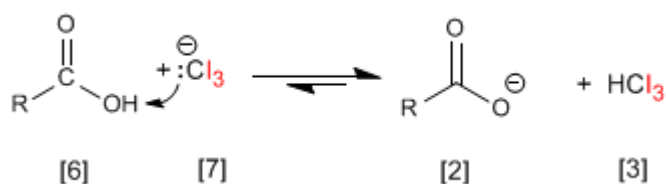
Las cetonas metílicas [1] reaccionan con halógenos en medios básicos generando carboxilatos [2] y haloformo [3].



El mecanismo consiste en halogenar completamente el metilo, sustituyendo en una etapa posterior el grupo -CX<sub>3</sub> formado por -OH.



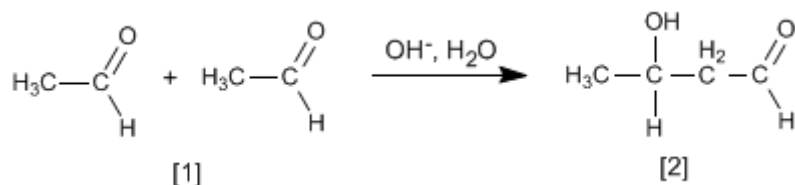
El grupo Cl<sub>3</sub><sup>-</sup> es muy básico y desprotona el ácido carboxílico formándose yodoformo y el carboxilato.



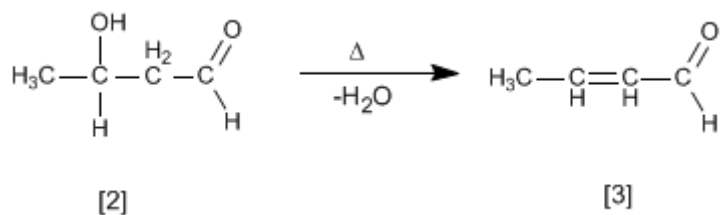
Esta reacción (con yodo) puede emplearse como ensayo analítico para identificar cetonas metílicas aprovechando que el yodoformo precipita de color amarillo.

## Condensación Aldólica

Aldehídos y cetonas [1] condensan en medios básicos formando aldoles [2]. Esta reacción se denomina condensación aldólica.

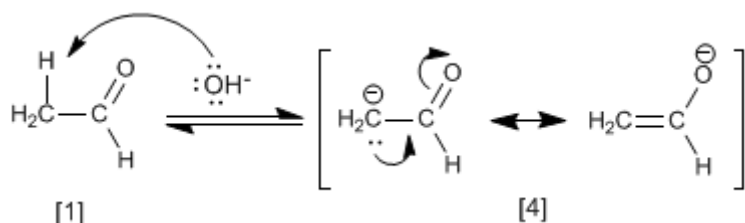


El aldol [2] formado deshidrata en el medio básico por calentamiento para formar un α,β-insaturado [3].



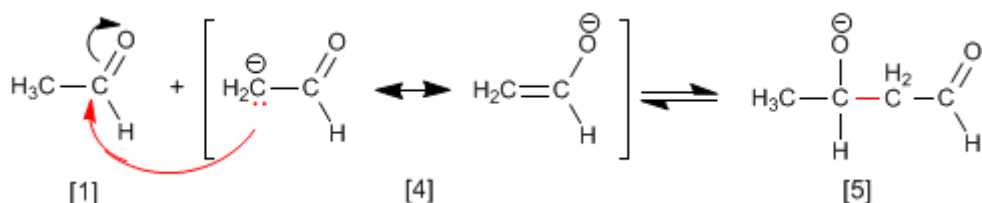
El mecanismo de la condensación aldólica transcurre con formación de un enolato, que ataca al carbonilo de otra molécula. En esta condensación se forma un enlace carbono-carbono entre el carbonilo de una molécula y el carbono  $\alpha$  de la otra.

### Etapas 1. Formación del enolato

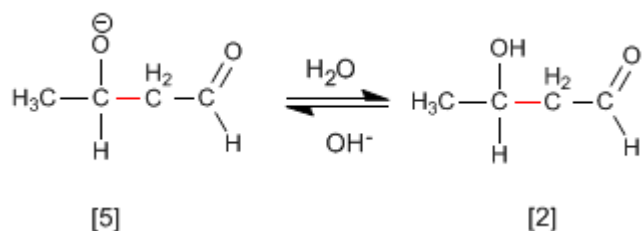


La base desprotona el carbono alfa del etanal [1] generando el enolato [4] estabilizado por resonancia.

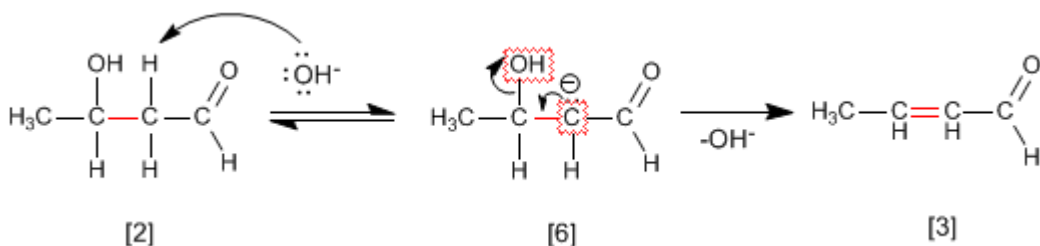
### Etapas 2. Ataque nucleófilo del enolato sobre el carbonilo



### Etapas 3. Protonación

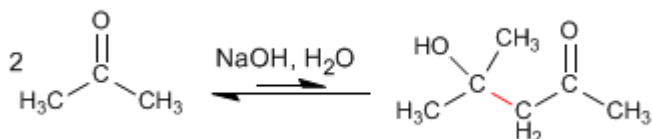


### Etapas 4. Deshidratación del aldol

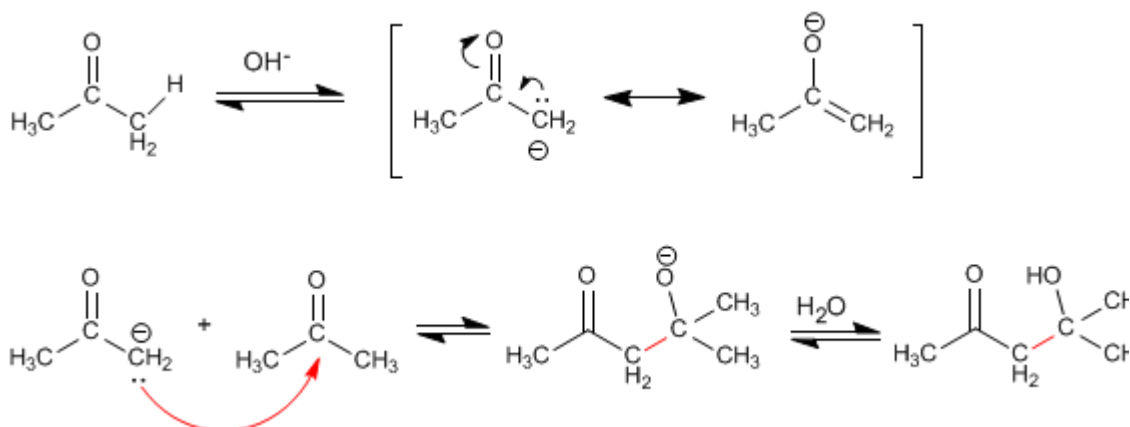


## Condensación aldólica con cetonas

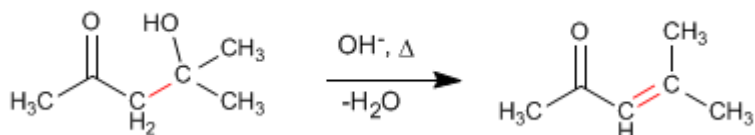
Las cetonas son menos reactivas que los aldehídos y dan un rendimiento muy bajo en la condensación aldólica. Así, dos moléculas de propanona condensan para formar el aldol correspondiente con un rendimiento del 2%. Se pueden conseguir porcentajes elevados del producto separándolo del medio de reacción según se va formando, o bien, calentando para deshidratarlo. De ambas formas los equilibrios de la aldólica se desplazan hacia el producto final.



**Mecanismo de la reacción:**

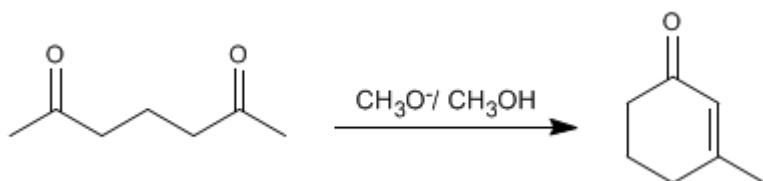


La deshidratación final permite el desplazamiento de los equilibrios. También se puede realizar una extracción del aldol del medio de reacción para favorecer la reacción.



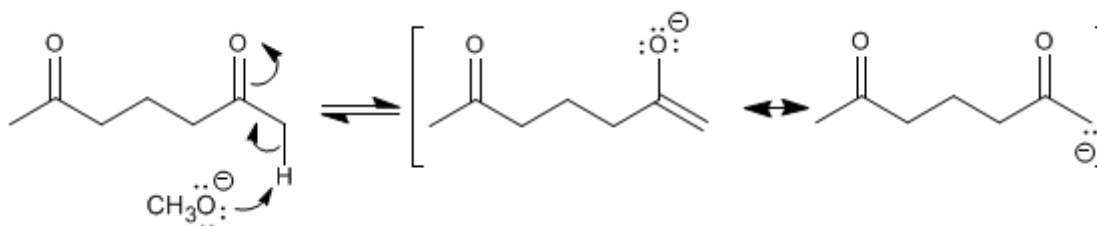
## Condensación aldólica intramolecular

Los compuestos dicarbonílicos condensan mediante la aldólica intramolecular en medios básicos. En esta reacción se obtienen ciclos de cinco o seis miembros. Así, la 2,6-heptanodiona condensa con metóxido en metanol para formar el 3-metilciclohex-2-enona.

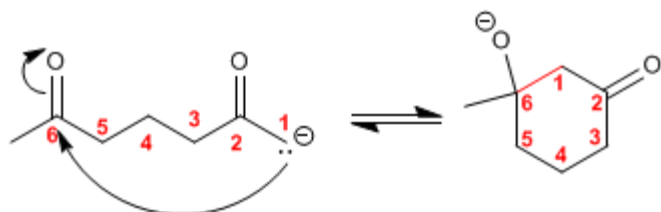


El mecanismo de la reacción transcurre a través de las siguientes etapas:

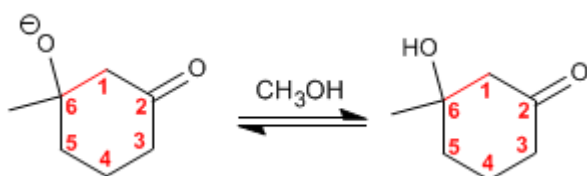
### Etapa 1. Formación del enolato.



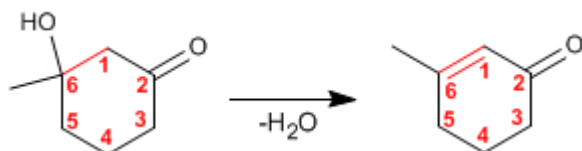
### Etapa 2. Adición nucleófila intramolecular



### Etapa 3. Protonación de la base del aldol



### Etapa 4. Deshidratación del aldol

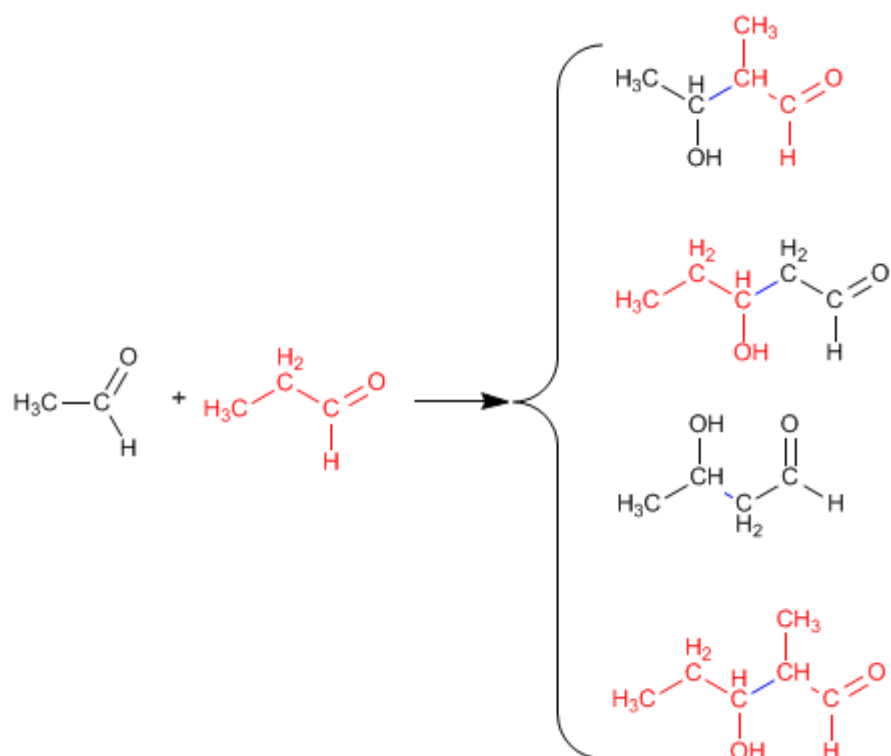


## Condensación aldólica cruzada o mixta

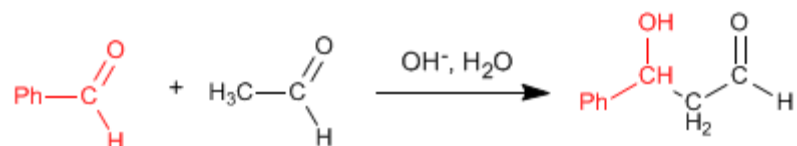
La reacción entre dos carbonilos diferentes se llama aldólica cruzada o mixta. Esta reacción sólo tiene utilidad sintética en dos casos:

1. Sólo uno de los carbonilos puede formar enolatos.
  2. Uno de los carbonilos es mucho más reactivo que el otro.
- En el resto de situaciones la aldólica mixta genera mezclas de cuatro productos. Veamos como ejemplo la condensación del etanal y propanal.



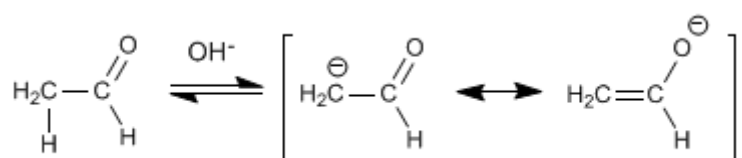


La condensación aldólica mixta del etanal con el benzaldehído genera un producto, cuando se trabaja en exceso de benzaldehído, debido a que el benzaldehído carece de hidrógenos en el carbono alfa y no puede formar enolatos.



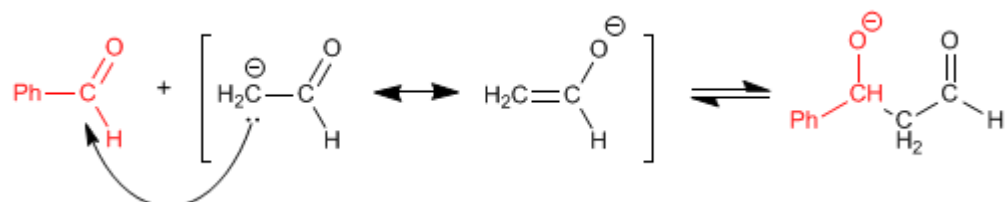
El mecanismo de esta reacción tiene lugar en las siguientes etapas:

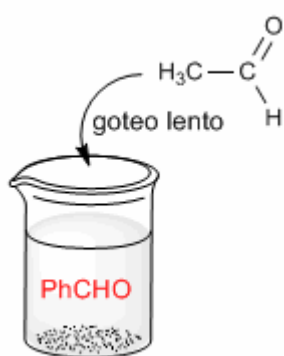
**Etapla 1.** Enolización del etanal



La formación de enolatos sólo puede tener lugar con el etanal, puesto que el benzaldehído carece de hidrógenos ácidos en el carbono alfa.

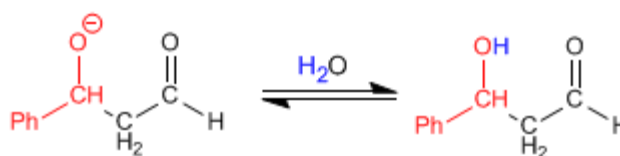
**Etapla 2.** Ataque nucleófilo del enolato al benzaldehído.





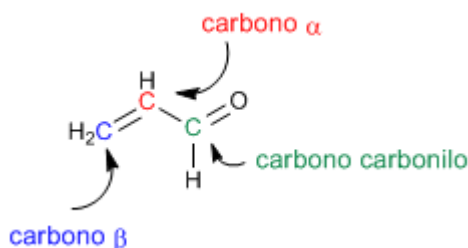
En esta etapa puede ocurrir el ataque del enolato de etanal sobre si mismo. Para evitarlo debe trabajarse en exceso de benzaldehído. Un procedimiento experimental muy usado para evitar la condensación del etanal consigo mismo es gotear lentamente el etanal sobre una disolución básica de benzaldehído

### Etapa 3. Protonación



## Síntesis de carbonilos alfa,beta-insaturados

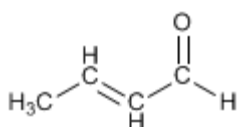
Los carbonilos  $\alpha,\beta$ -insaturados son compuestos orgánicos que tienen un doble enlace entre las posiciones  $\alpha,\beta$  de un aldehído o cetona.



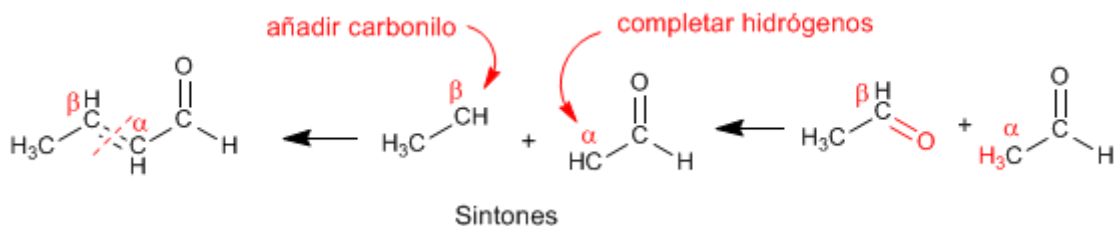
El propenal o acroleína es un carbonilo  $\alpha,\beta$ -insaturado. Sus dos dobles enlaces conjugados le confieren una reactividad especial.

Existen 4 métodos importantes para la preparación de  $\alpha,\beta$ -insaturados: condensación aldólica, halogenación del carbono  $\alpha$  seguida de eliminación, oxidación de alcoholes alílicos y Wittig.

**Método 1.** Preparar mediante la condensación aldólica el siguiente compuesto.

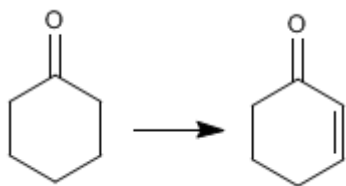


Empleamos la retrosíntesis para preparar el compuesto. Al ser de la familia de los  $\alpha,\beta$ -insaturados se puede obtener mediante la condensación aldólica.

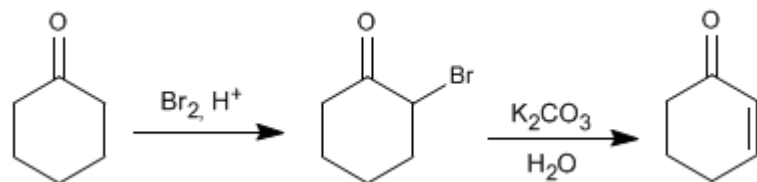


Para obtener los reactivos que forman el  $\alpha,\beta$ -insaturado se rompe por el doble enlace, obteniéndose los sintones (equivalentes sintéticos). Los reactivos se obtienen añadiendo al carbono  $\beta$  un carbonilo y completando los hidrógeno que faltan en el carbono  $\alpha$ .

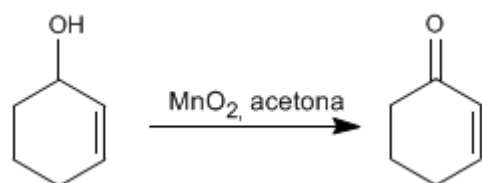
**Ejemplo 2.** Indicar como se puede realizar las siguiente transformación.



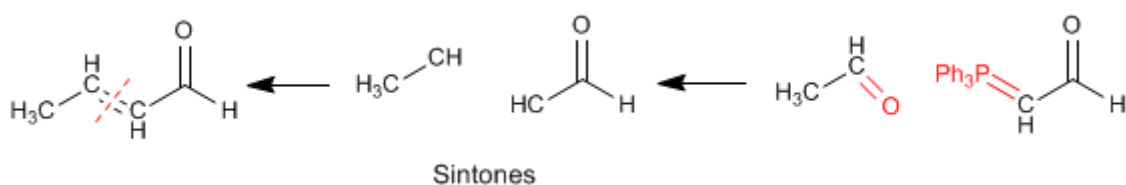
En una primera etapa se halogena la posición  $\alpha$  del carbonilo. En la segunda etapa se realiza una eliminación que nos deja el producto final.



**Método 3.** La oxidación de alcoholes alílicos con dióxido de manganeso en acetona produce  $\alpha,\beta$ -insaturados

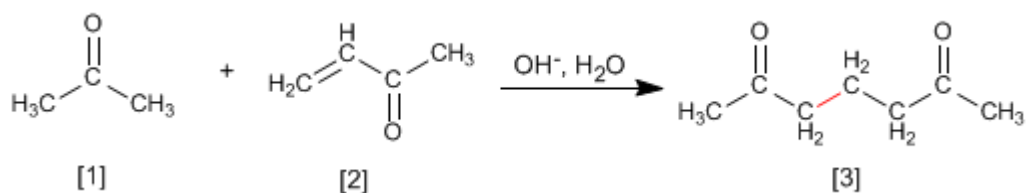


**Método 4.** Reacción de Wittig



## Adición de Michael y anelación de Robinson

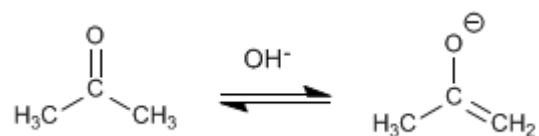
Los enolatos de aldehídos o cetonas se adicionan a los  $\alpha,\beta$ -insaturados para formar 1,5-dicarbonilos. Esta reacción se denomina adición de Michael.



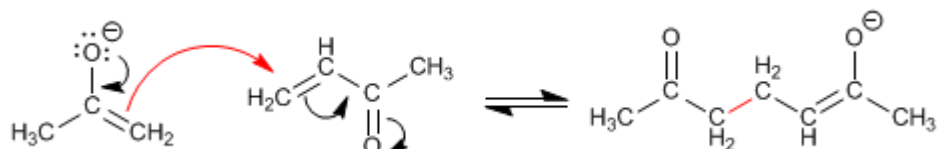
La propanona [1] reacciona con el  $\alpha,\beta$ -insaturado [2] para formar el 1,5-dicarbonilo [3]

Mecanismo de la Adición de Michael:

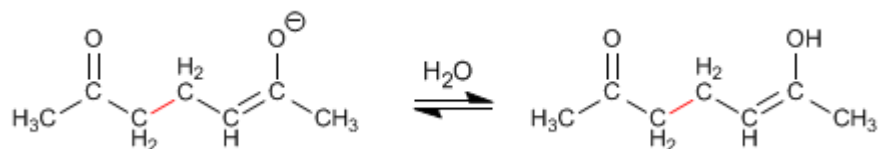
**Etapas 1.** Formación del enolato.



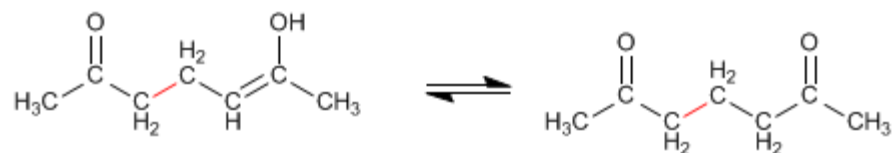
**Etapas 2.** Ataque nucleófilo del enolato al carbono  $\beta$  del  $\alpha,\beta$ -insaturado.



**Etapas 3.** Equilibrio ácido-base



**Etapas 4.** Tautomería ceto-enol



El producto de Michael puede condensar mediante una aldólica intramolecular, formando un  $\alpha,\beta$ -insaturado. El conjunto de la adición de Michael y la aldólica final se conoce como reacción de Robinson

*Chemsoft ®*

# *Química Orgánica*

*Recopilación : 2da Edición - 2009*

*José A.*

# *Química Orgánica*

*Recopilación: 2da Edición*

*Diciembre 2009*

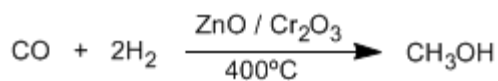
## *Índice:*

- i. Alcoholes*
- ii. Éteres*
- iii. Aldehídos y Cetonas*
- iv. Enoles y Enolatos*
- v. Benceno*

## SÍNTESIS Y REACTIVIDAD DE ALCOHOLES

### Alcoholes - características generales

Los alcoholes son compuesto orgánicos que contienen el grupo hidroxilo (-OH). El metanol es el alcohol más sencillo, se obtiene por reducción del monóxido de carbono con hidrógeno.

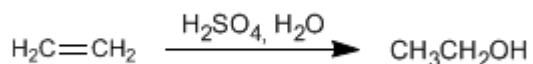


El metanol es un líquido incoloro, su punto de ebullición es 65°C, miscible en agua en todas las proporciones y venenoso (35 ml pueden matar una persona)

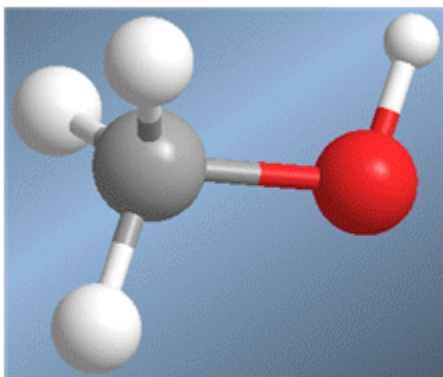
La mitad del metanol producido se oxida a metanal (formaldehído), material de partida para la fabricación de resinas y plásticos.

El etanol se obtiene por fermentación de materia vegetal, obteniéndose una concentración máxima de 15% en etanol. Por destilación se puede aumentar esta concentración hasta el 98%.

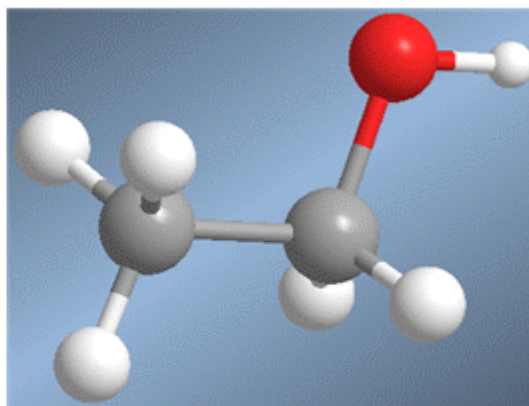
También se puede obtener etanol por hidratación del etileno (eteno) que se obtiene a partir del petróleo.



El etanol es un líquido incoloro, miscible en agua en todas proporciones, con punto de ebullición de 78°C. Es fácilmente metabolizado por nuestros organismos, aunque su abuso causa alcoholismo.



(metanol)  $\text{CH}_3\text{OH}$

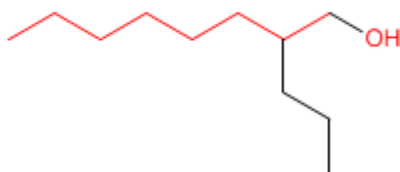
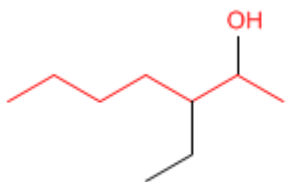


(etanol)  $\text{CH}_3\text{CH}_2\text{OH}$

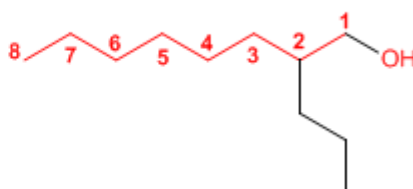
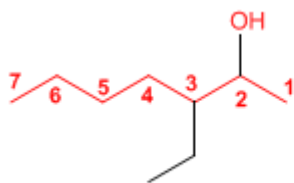


## Nomenclatura de Alcoholes

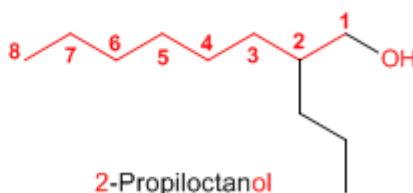
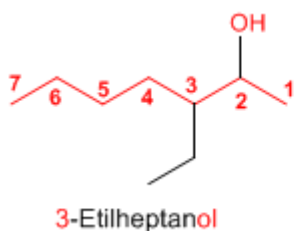
**Regla 1.** Se elige como cadena principal la de mayor longitud que contenga el grupo -OH.



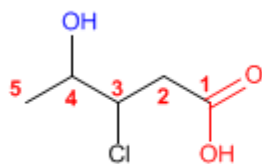
**Regla 2.** Se numera la cadena principal para que el grupo -OH tome el localizador más bajo. El grupo hidroxilo tiene preferencia sobre cadenas carbonadas, halógenos, dobles y triples enlaces.



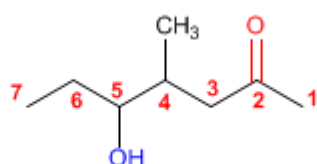
**Regla 3.** El nombre del alcohol se construye cambiando la terminación -o del alcano con igual número de carbonos por -ol



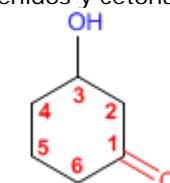
**Regla 4.** Cuando en la molécula hay grupos funcionales de mayor prioridad, el alcohol pasa a ser un mero sustituyente y se llama **hidroxi-**. Son prioritarios frente a los alcoholes: ácidos carboxílicos, anhídridos, ésteres, haluros de alcanoilo, amidas, nitrilos, aldehídos y cetonas.



Ácido 3-cloro-4-hidroxi-pentanoico

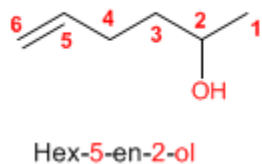


5-Hidroxi-4-metilheptanona

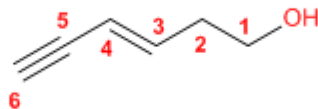


3-Hidroxiciclohexanona

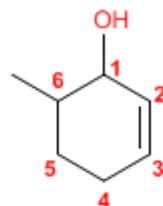
**Regla 5.** El grupo -OH es prioritario frente a los alquenos y alquinos. La numeración otorga el localizador más bajo al -OH y el nombre de la molécula termina en -ol.



Hex-5-en-2-ol



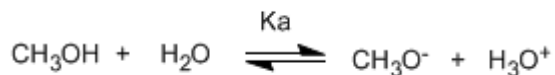
Hex-3-en-5-in-1-ol



6-Metilciclohex-2-en-1-ol

## Acidez y basicidad de alcoholes

Los alcoholes son especies anfóteras (anfipróticas), pueden actuar como ácidos o bases. En disolución acuosa se establece un equilibrio entre el alcohol, el agua y sus bases conjugadas.



Escribiendo la constante del equilibrio ( $K_a$ )

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{O}^-]}{[\text{CH}_3\text{OH}]} = 10^{-15.5}$$

El pequeño valor de la constante nos indica que el equilibrio está totalmente desplazado a la izquierda.

El logaritmo cambiado de signo de la constante de equilibrio nos da el  $pK_a$  del metanol, parámetro que indica el grado de acidez de un compuesto orgánico.

$$pK_a = -\log k_a = 15.5$$

El aumento del  $pK_a$  supone una disminución de la acidez. Así, el metanol con un  $pK_a$  de 15.5 es ligeramente más ácido que el etanol con  $pK_a$  de 15.9.

El  $pK_a$  de los alcoholes se ve influenciado por algunos factores como son el tamaño de la cadena carbonada y los grupos electronegativos

Al aumentar el tamaño de la cadena carbonada el alcohol se vuelve menos ácido.

$\text{CH}_3\text{OH}$	$pK_a = 15.5$	
$\text{CH}_3\text{CH}_2\text{OH}$	$pK_a = 15.9$	
$(\text{CH}_3)_2\text{CHOH}$	$pK_a = 17.1$	
$(\text{CH}_3)_3\text{COH}$	$pK_a = 18$	

Los grupos electronegativos (halógenos) aumentan la acidez de los alcoholes (bajan el  $pK_a$ )

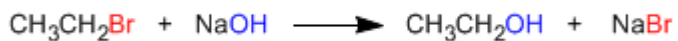
$\text{CH}_3\text{CH}_2\text{OH}$	$pK_a = 15.9$	
$\text{ClCH}_2\text{CH}_2\text{OH}$	$pK_a = 14.3$	
$\text{F}_3\text{CCH}_2\text{OH}$	$pK_a = 12.4$	

## Síntesis de Alcoholes a partir de Haloalcanos

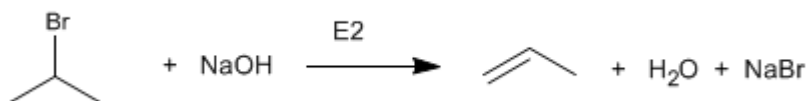
Los alcoholes se pueden obtener a partir de haloalcanos mediante reacciones  $S_N2$  y  $S_N1$

### Síntesis de alcoholes mediante $S_N2$

Los haloalcanos primarios reaccionan con hidróxido de sodio para formar alcoholes. Haloalcanos secundarios y terciarios eliminan para formar alquenos.

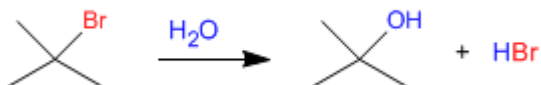


El bromuro de isopropilo (sustrato secundario) elimina al reaccionar con el ión hidróxido.



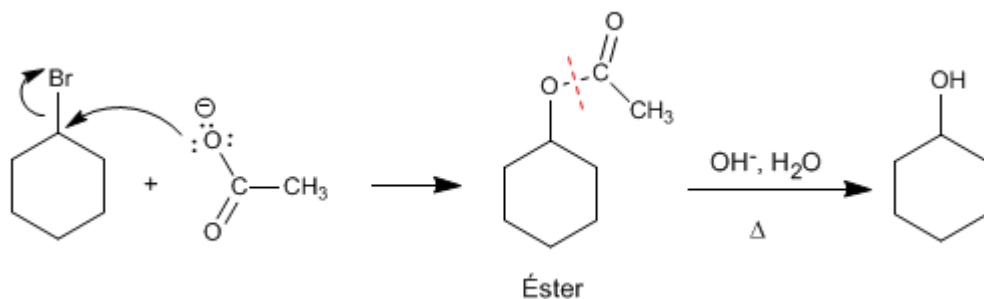
### Síntesis de alcoholes mediante $S_N1$

Los sustratos secundarios y terciarios reaccionan con agua mediante mecanismo  $S_N1$  para formar alcoholes.



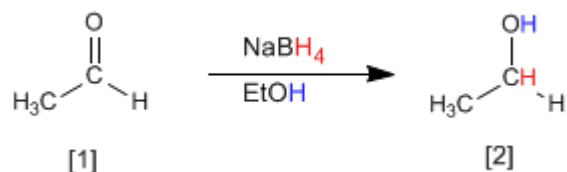
### Hidrólisis de ésteres

Es un método interesante para preparar alcoholes a partir de haloalcanos secundarios. El haloalcano se convierte en éster por reacción con acetato de sodio, para después hidrolizarse en medio ácido o básico, obteniéndose el alcohol.



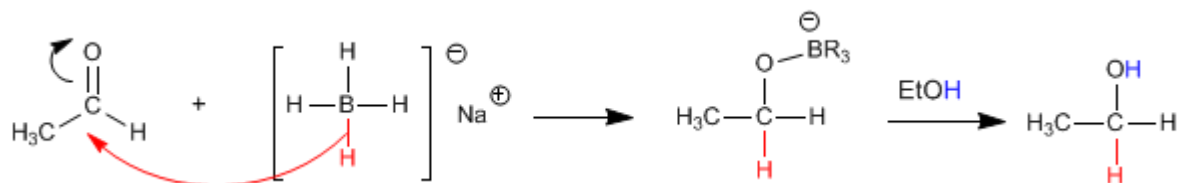
## Síntesis de Alcoholes por reducción de carbonilos

Tanto el borohidruro de sodio ( $\text{NaBH}_4$ ) como el hidruro de litio y aluminio ( $\text{LiAlH}_4$ ) reducen aldehídos y cetonas a alcoholes.

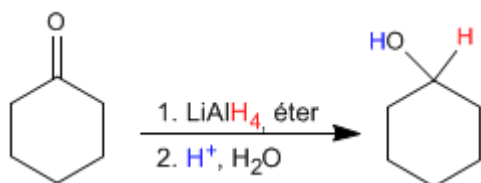


El etanal [1] se transforma por reducción con el borohidruro de sodio en etanol [2].

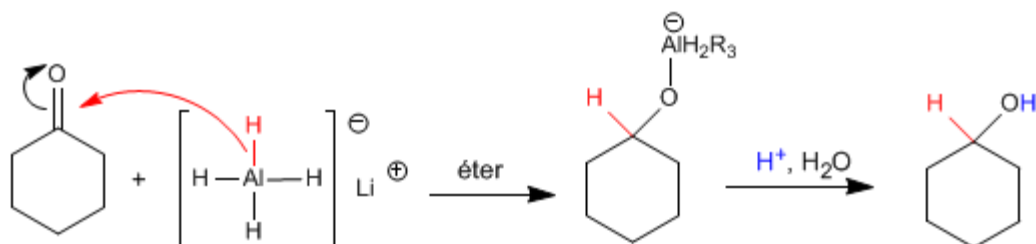
El mecanismo transcurre por ataque del hidruro procedente del reductor sobre el carbono carbonilo. En una segunda etapa el disolvente protona el oxígeno del alcóxido.



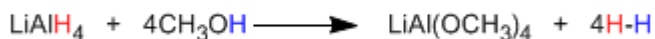
El hidruro de litio y aluminio trabaja en medio éter y transforma aldehídos y cetonas en alcoholes después de una etapa de hidrólisis ácida.



El mecanismo es análogo al del borohidruro de sodio.



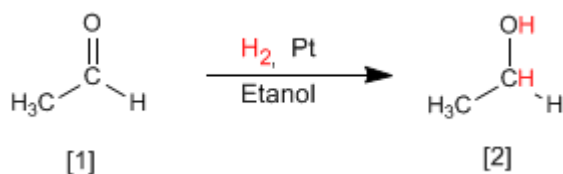
El reductor de litio y aluminio es más reactivo que el de boro, reacciona con el agua y los alcoholes desprendiendo hidrógeno. Por ello, debe disolverse en medios apróticos (éter).



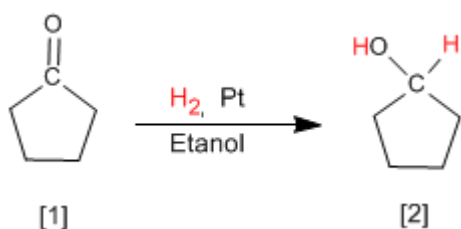
El reductor de boro, menos reactivo, descompone lentamente en medios próticos, lo que permite utilizarlo disuelto en etanol o agua.

## Síntesis de Alcoholes por hidrogenación de Carbonilos

Otro método para preparar alcoholes consiste en la reducción de aldehídos o cetonas a alcoholes. El método más simple es la hidrogenación del doble enlace carbono-oxígeno, utilizando hidrógeno en presencia de un catalizador de platino, paladio, níquel o rutenio.



El etanal [1] se transforma por hidrogenación del doble enlace en etanol [2]



La ciclopentanona [1] se transforma por hidrogenación en ciclopentanol [2]

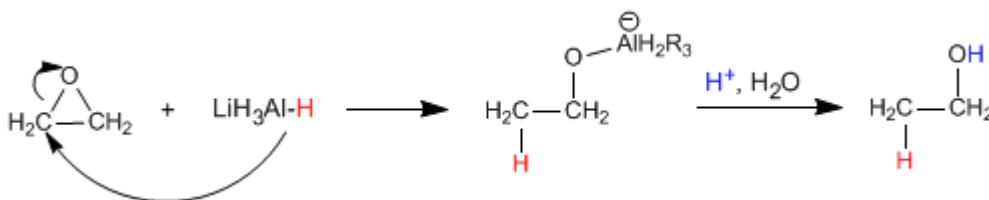
## Síntesis de Alcoholes a partir de Epóxidos

Los alcoholes se pueden obtener por apertura de epóxidos (oxaciclopropanos). Esta apertura se puede realizar empleando reactivos organometálicos o el reductor de litio y aluminio.



El oxaciclopropano [1] se transforma por reducción con hidruro de litio y aluminio en etanol [2].

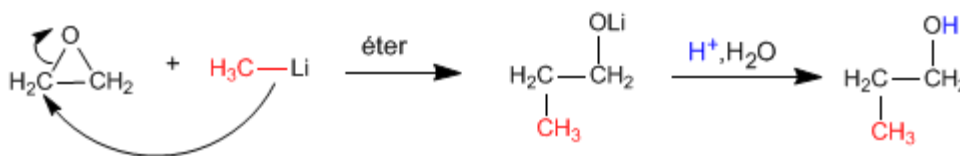
El mecanismo de la reacción comienza con el ataque del hidruro procedente del reductor sobre el carbono polarizado positivamente del epóxido, para terminar con la protonación del alcóxido.



Los reactivos de Grignard (organometálicos de magnesio) y los organolitílicos reaccionan con oxaciclopropano para dar un alcohol primario.



El metillitio ataca al oxaciclopropano [1] para formar propan-1-ol [2].

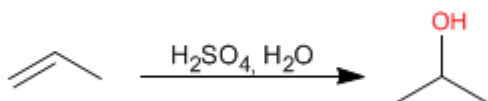


## Síntesis de Alcoholes por Hidratación de Alquenos

Un método de síntesis para alcoholes, ya estudiado en la sección de alquenos, consiste en hidratar el alqueno. La adición del -OH puede ser en el carbono más sustituido del alqueno (Markovnikov), o bien, en el carbono menos sustituido (antiMarkovnikov).

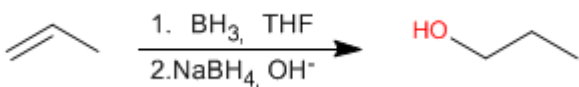
### Hidratación Markovnikov

En esta hidratación el grupo hidroxilo va al carbono con más sustituyentes. Se emplea como reactivo sulfúrico acuoso, o bien, acetato de mercurio en agua, seguido de reducción con borohidruro de sodio.



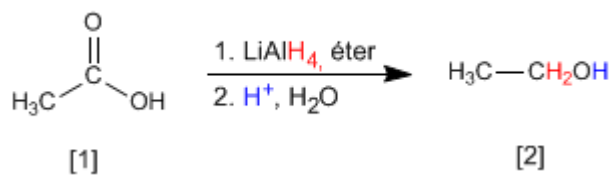
### Hidratación antiMarkovnikov

El grupo hidroxilo se adiciona al carbono menos sustituido. El reactivo empleado es borano en THF seguido de oxidación con agua oxigenada en medio básico (hidroboración)



## Síntesis de alcoholes por reducción de ácidos y ésteres

Los ácidos carboxílicos y los ésteres se reducen a alcoholes con el hidruro de litio y aluminio.  
Reductores más suaves como el borohidruro de sodio son incapaces de reducir estos compuestos.



El ácido etanoico [1] se transforma por reducción con hidruro de litio y aluminio en etanol [2].

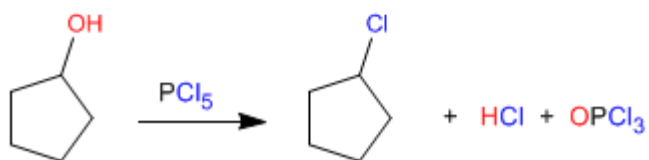
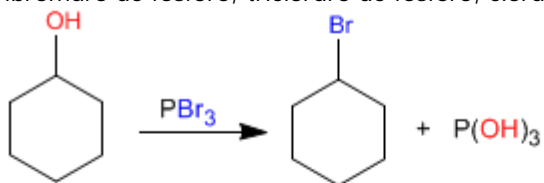


El benzoato de metilo [1] se transforma en alcohol bencílico [2] por reducción con hidruro de litio y aluminio.

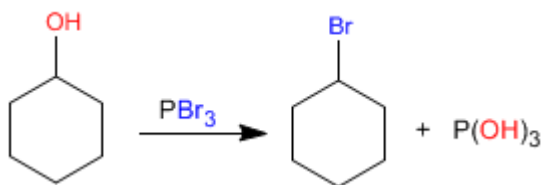


## Síntesis de Haloalcanos a partir de Alcoholes

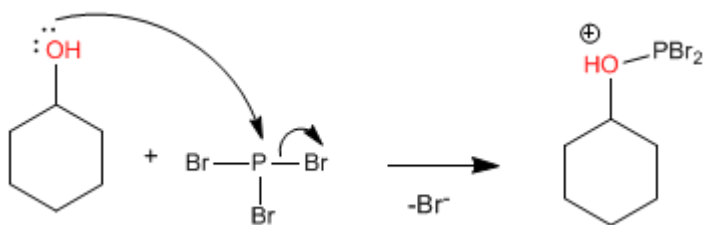
Los alcoholes primarios y secundarios pueden convertirse en haloalcanos con reactivos como: tribromuro de fósforo, tricloruro de fósforo, cloruro de tionilo y pentacloruro de fósforo.



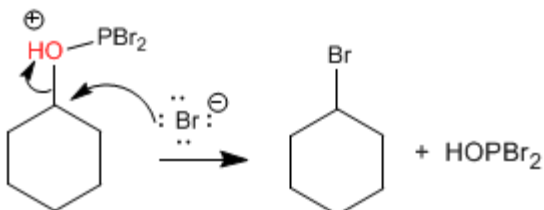
El mecanismo de estas reacciones es de tipo  $\text{S}_{\text{N}}2$  y sólo los alcoholes primarios y secundarios reaccionan. Veamos el mecanismo de la primera reacción.



**Etapas 1.** Ataque del alcohol al tribromuro de fósforo



**Etapas 2.** Sustitución nucleófila bimolecular, actuando el bromuro como nucleófilo

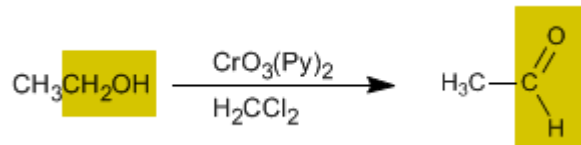


Todos los bromos del  $\text{PBr}_3$  son reactivos y el mecanismo se repite dos veces más.

## Oxidación de Alcoholes

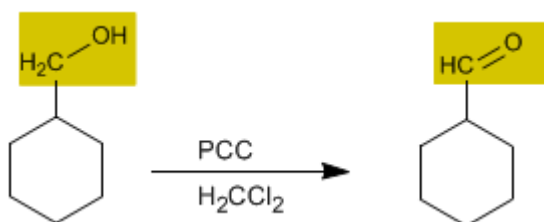
La oxidación de alcoholes forma compuestos carbonilos. Al oxidar alcoholes primarios se obtienen aldehídos, mientras que la oxidación de alcoholes secundarios forma cetonas.

### Oxidación de alcoholes primarios a aldehídos



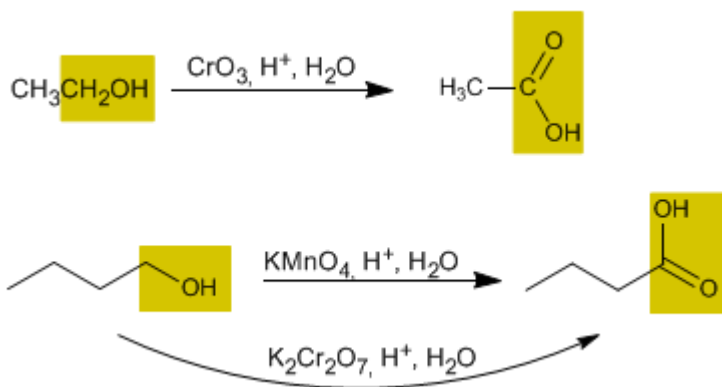
El trióxido de cromo con piridina en diclorometano permite aislar aldehídos con buen rendimiento a partir de alcoholes primarios.

Se conoce como PCC (clorocromato de piridinio) al trióxido de cromo con piridina y ácido clorhídrico en diclorometano. Este reactivo también convierte alcoholes primarios en aldehídos.



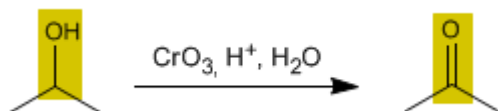
### Oxidación de alcoholes primarios a ácidos carboxílicos

El trióxido de cromo en medio ácido acuoso (reactivo de Jones), el permanganato de potasio y el dicromato de potasio oxidan los alcoholes primarios a ácidos carboxílicos.



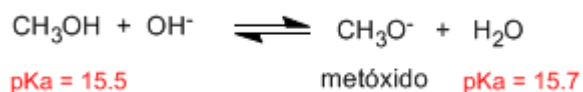
### Oxidación de alcoholes secundarios a cetonas

Los oxidantes convierten los alcoholes secundarios en cetonas. No es posible la sobreoxidación a ácido carboxílico.

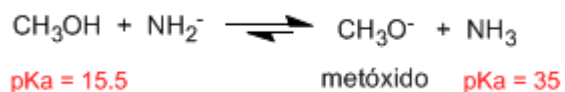


## Formación de Alcóxidos a partir de Alcoholes

Los alcóxidos son las bases de los alcoholes, se obtienen por reacción del alcohol con una base fuerte.

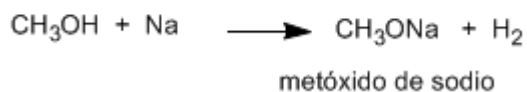
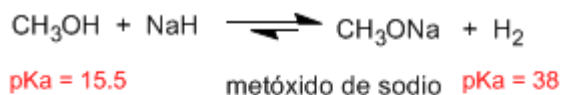


Los  $\text{pK}_a$  de los ácidos conjugados son similares y el equilibrio no se encuentra desplazado. El ión hidróxido es una base demasiado débil para formar el alcóxido en cantidad importante.



El amiduro es una base muy fuerte y desplaza el equilibrio a la derecha, transformando el metanol en metóxido.

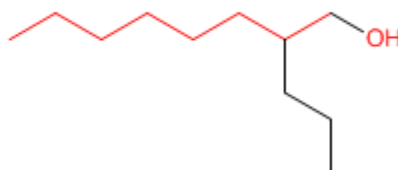
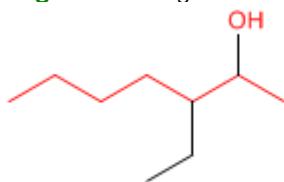
Otras bases fuertes que pueden ser usadas para formar alcóxidos son: hidruro de sodio, LDA, sodio metal.



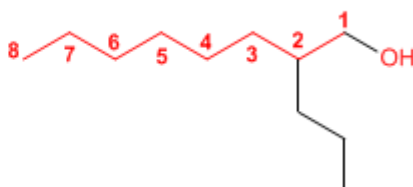
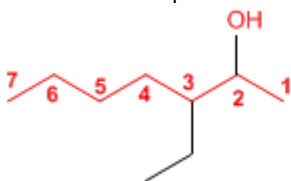
## PROBLEMAS NOMENCLATURA - ALCOHOLES

### Nomenclatura de Alcoholes - Reglas IUPAC

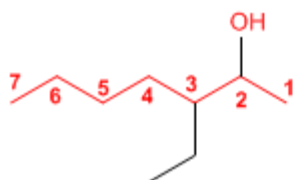
**Regla 1.** Se elige como cadena principal la de mayor longitud que contenga el grupo -OH.



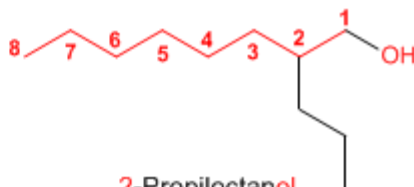
**Regla 2.** Se numera la cadena principal para que el grupo -OH tome el localizador más bajo. El grupo hidroxilo tiene preferencia sobre cadenas carbonadas, halógenos, dobles y triples enlaces.



**Regla 3.** El nombre del alcohol se construye cambiando la terminación -o del alcano con igual número de carbonos por -ol.

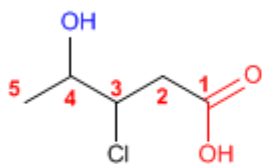


3-Etilheptanol

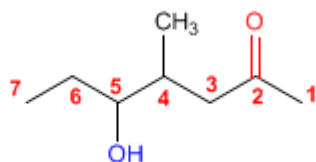


2-Propiloctanol

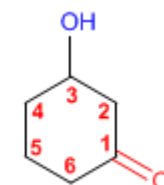
**Regla 4.** Cuando en la molécula hay grupos funcionales de mayor prioridad, el alcohol pasa a ser un mero sustituyente y se llama **hidroxi-**. Son prioritarios frente a los alcoholes: ácidos carboxílicos, anhídridos, ésteres, haluros de alcanoilo, amidas, nitrilos, aldehídos y cetonas.



Ácido 3-cloro-4-hidroxipentanoico

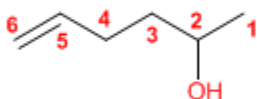


5-Hidroxi-4-metilheptanona

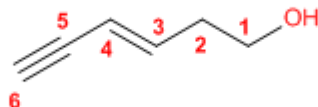


3-Hidroxiciclohexanona

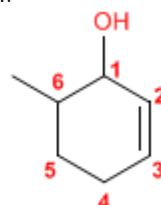
**Regla 5.** El grupo -OH es prioritario frente a los alquenos y alquinos. La numeración otorga el localizador más bajo al -OH y el nombre de la molécula termina en -ol.



Hex-5-en-2-ol



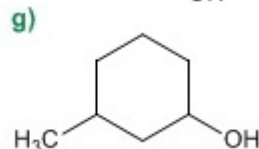
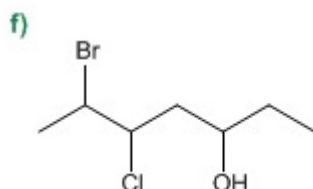
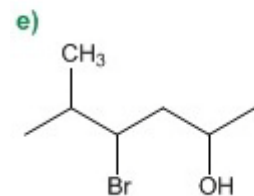
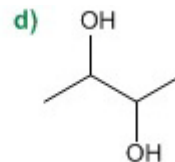
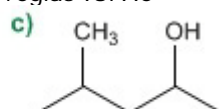
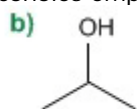
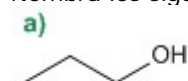
Hex-3-en-5-in-1-ol



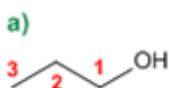
6-Metilciclohex-2-en-1-ol

## Nomenclatura de Alcoholes - Problema 0.1

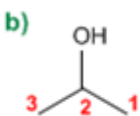
Nombra los siguientes alcoholes empleando reglas IUPAC



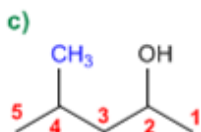
### Solución:



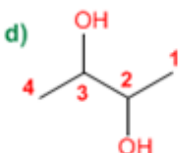
1. Cadena principal: la de mayor longitud que contenga el -OH (propano)
2. Numeración: otorga al -OH el localizador más bajo.
3. Sustituyentes: no
4. Nombre: Propan-1-ol



1. Cadena principal: la de mayor longitud que contenga el -OH (propano)
2. Numeración: indiferente.
3. Sustituyentes: no
4. Nombre: Propan-2-ol



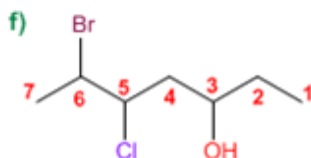
1. Cadena principal: la de mayor longitud que contenga el -OH (pentano)
2. Numeración: otorga al -OH el localizador más bajo (-OH preferente sobre cadenas)
3. Sustituyentes: metilo en 4
4. Nombre: 4-Metilpentan-2-ol



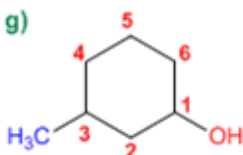
1. Cadena principal: mayor longitud (butano)
2. Numeración: comienza en uno de los extremos.
3. Sustituyentes: no
4. Nombre: Butano-2,3-diol



1. Cadena principal: mayor longitud (hexano)
2. Numeración: comienza en el extremo derecho, para otorgar al -OH el localizador más bajo.
3. Sustituyentes: bromo en posición 4 y metilo en 5.
4. Nombre: 4-Bromo-5-metilhexan-2-ol



1. Cadena principal: mayor longitud (heptano)
2. Numeración: comienza en extremo que otorga el localizador más bajo al -OH.
3. Sustituyentes: bromo en 6 y cloro en 5.
4. Nombre: 6-Bromo-5-cloroheptan-3-ol



1. Cadena principal: ciclo de seis miembros (ciclohexano)
2. Numeración: comienza en el carbono del -OH.
3. Sustituyentes: metilo en 3.
4. Nombre: 3-Metilciclohexanol

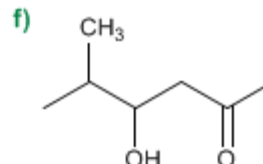
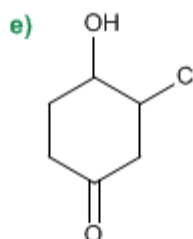
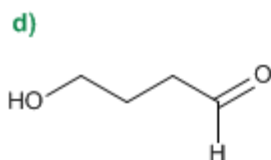
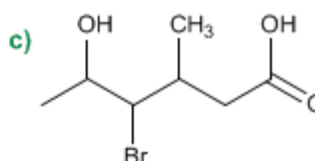
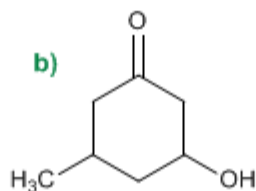
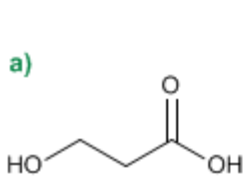
1. Cuando en una molécula hay más de un grupo -OH se pueden emplear los prefijos de cantidad di, tri, tetra, penta, hexa,..... La numeración debe otorgar los menores localizadores a los -OH.

2. El nombre del alcohol se construye comenzando por los sustituyentes, precedidos por sus respectivos localizadores, terminando en el nombre de la cadena principal. La terminación -o del alcano correspondiente se sustituye por -ol.

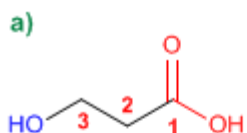
3. En el caso de alcoholes cíclicos no es necesario indicar la posición del grupo hidroxilo, puesto que siempre toma localizador 1.

## Nomenclatura de Alcoholes - Problema 0.2

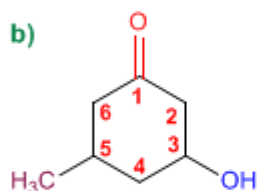
Nombra los siguientes moléculas, en las que el alcohol actúa como sustituyente.



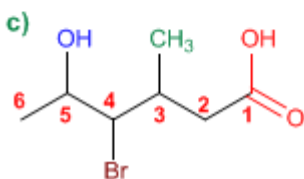
Solución



1. Cadena principal: más larga que contenga el grupo funcional (propano)
2. Grupo funcional: ácido carboxílico
3. Numeración: localizador más bajo al grupo ácido
4. Sustituyentes: grupo **hidroxi** en 3.
5. Nombre: **Acido 3-hidroxi**propanoico



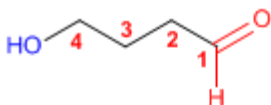
1. Cadena principal: ciclo de seis miembros (ciclohexano)
2. Grupo funcional: cetona
3. Numeración: localizador más bajo al grupo carbonilo
4. Sustituyentes: grupo **hidroxi** en 3 y **metilo** en 4.
5. Nombre: **2-Hidroxi-5-metil**ciclohexan**ona**



1. Cadena principal: más larga que contenga el grupo funcional (hexano)
2. Grupo funcional: ácido carboxílico
3. Numeración: asigna el localizador más bajo al grupo ácido.
4. Sustituyentes: **bromo** en 4, grupo **hidroxi** en 5 y **metilo** en 3
5. Nombre: **Acido 4-bromo-6-hidroxi-3-metil**hexano**ico**

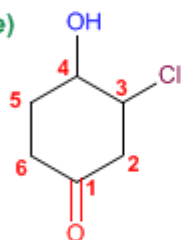
Los ácidos carboxílicos y las cetonas son prioritarios sobre los alcoholes.  
El alcohol pasa a ser un sustituyente más de la molécula, ordenándose alfabéticamente con el resto de sustituyentes.

d)



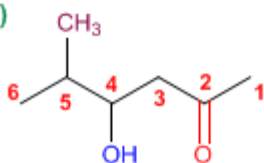
1. Cadena principal: más larga que contenga el grupo funcional (butano)
2. Grupo funcional: aldehído
3. Numeración: localizador más bajo al grupo carbonilo
4. Sustituyentes: grupo **hidroxi** en 4.
5. Nombre: **4-Hidroxibutanal**

e)



1. Cadena principal: ciclo de seis miembros
2. Grupo funcional: cetona
3. Numeración: localizador más bajo al carbonilo
4. Sustituyentes: **cloro** en 3 e **hidroxi** en 4.
5. Nombre: **3-Cloro-4-hidroxiciclohexanona**

f)



1. Cadena principal: más larga que contenga el grupo funcional (propano)
2. Grupo funcional: cetona
3. Numeración: localizador más bajo al grupo carbonilo
4. Sustituyentes: grupo **hidroxi** en 4 y **metilo** en 5.
5. Nombre: **3-Hidroxi-4-metilhexan-2-ona**

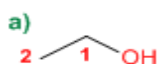


## Nomenclatura de Alcoholes - Problema 0.3

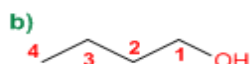
Dibujar la estructura de los siguientes alcoholes:

- |                          |                                   |
|--------------------------|-----------------------------------|
| a) Etanol                | i) Ciclopent-2-enol               |
| b) Butanol               | j) 2,3-Dimetilciclohexanol        |
| c) 2-Metilpropan-1-ol    | k) Octa-3,5-dien-2-ol             |
| d) 2-Metilbutan-2-ol     | l) Hex-4-en-1-in-3-ol             |
| e) 3-Metilbutan-2-ol     | m) 2-Bromohept-2-en-1,4-diol      |
| f) 3-Metilbutan-1-ol     | n) 2-Fenil-5-metilheptan-2-ol     |
| g) 2,3-Pentanodiol       | o) Alcohol bencílico              |
| h) 2-Etil-pent-3-en-1-ol | p) 1,2,3-Propanotriol (glicerina) |

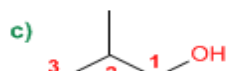
### Solución:



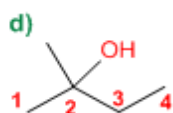
Etanol



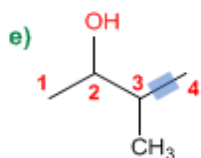
Butanol



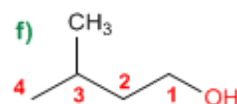
2-Metilpropan-1-ol



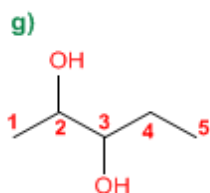
2-Metilbutan-2-ol



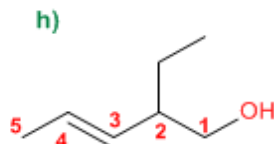
3-Metilbutan-2-ol



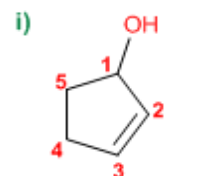
3-Metilbutan-1-ol



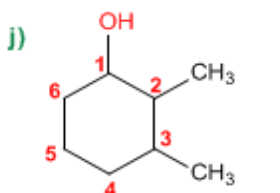
2,3-Pentanodiol



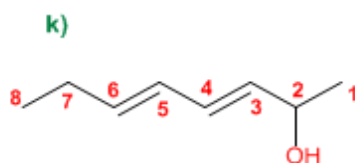
2-Etil-pent-3-en-1-ol



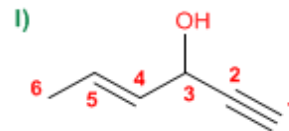
Ciclopent-2-enol



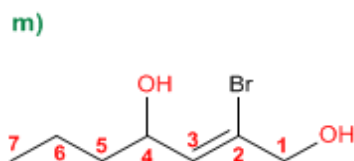
2,3-Dimetilciclohexanol



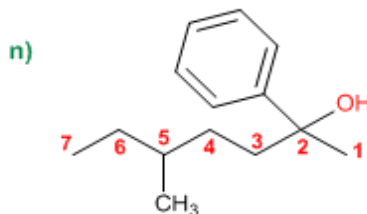
Octa-3,5-dien-2-ol



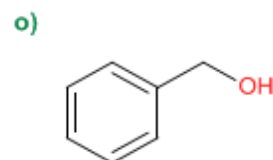
Hex-4-en-1-in-3-ol



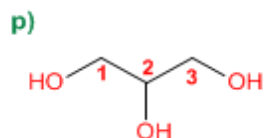
2-Bromohept-2-en-1,4-diol



2-Fenil-5-metilheptan-2-ol



Alcohol bencílico

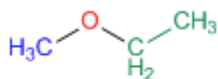


1,2,3-Propanotriol (glicerina)

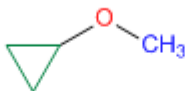
## TEORÍA DE ÉTERES

### Nomenclatura de éteres - epóxidos

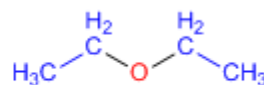
La nomenclatura de los éteres consiste en nombrar alfabéticamente los dos grupos alquilo que parten del oxígeno, terminando el nombre en éter. Veamos algunos ejemplos:



Etil metil éter

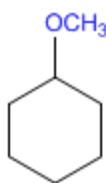


Ciclopropil metil éter

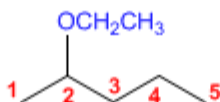


Dietil éter

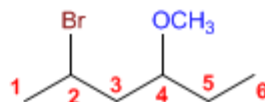
También se pueden nombrar los éteres como grupos alcoxi.



Metóxiciclohexano



2-Etoxi pentano

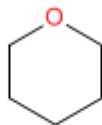


2-Bromo-4-metoxihexano

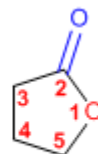
Los éteres cíclicos se forman sustituyendo  $-CH_2-$  del ciclo por  $-O-$ . Este cambio se indica con el prefijo **oxa-**.



Oxaciclopropano



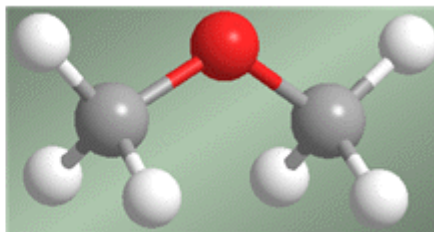
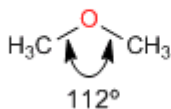
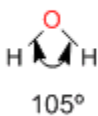
Oxaciclohexano



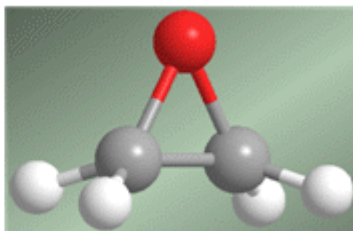
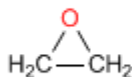
2-oxo-oxaciclopentano

## Estructura y enlace en éteres y epóxidos

Los éteres son moléculas de estructura similar al agua y alcoholes. El ángulo entre los enlaces C-O-C es mayor que en el agua debido a las repulsiones estéricas entre grupos voluminosos.

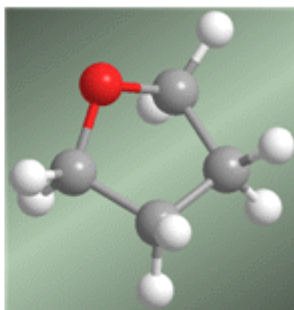
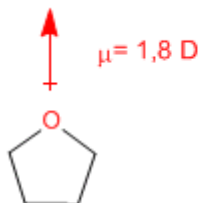


En el caso de los epóxidos la característica más relevante es la tensión del anillo, debida a ángulos de enlace muy distantes a los  $109^\circ$ .



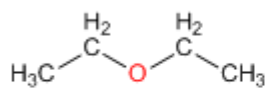
El enlace C-O-C presenta un ángulo de  $61^\circ$ .

Los éteres son moléculas muy polares. Así, el Dietil éter presenta un momento dipolar de 1,2 D. Este momento dipolar es aún más importante en éteres cíclicos (oxaciclopropano, tetrahidrofurano) que presentan momentos dipolares sobre 1,8 D, similares al agua.



## Propiedades físicas de los éteres

Los éteres presentan unos puntos de ebullición inferiores a los alcoholes, aunque su solubilidad en agua es similar. Dada su importante estabilidad en medios básicos, se emplean como disolventes inertes en numerosas reacciones.

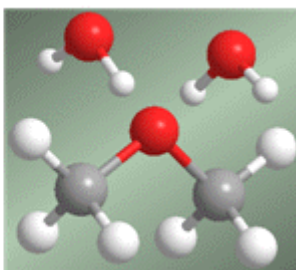
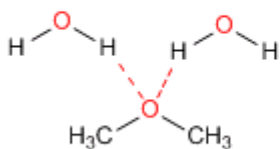


Dietil éter

P. ebul = 35°C

Solubilidad agua = 7,5 g/100ml

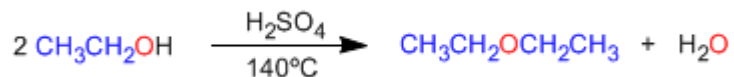
La importante solubilidad en agua se explica por los puentes de hidrógeno que se establecen entre los hidrógenos del agua y el oxígeno del éter.



## Síntesis de éteres por condensación de alcoholes

### 1. Éteres a partir de alcoholes primarios

Los éteres simétricos pueden prepararse por condensación de alcoholes. La reacción se realiza bajo calefacción (140°C) y con catálisis ácida. Así, dos moléculas de etanol condensan para formar dietil éter.

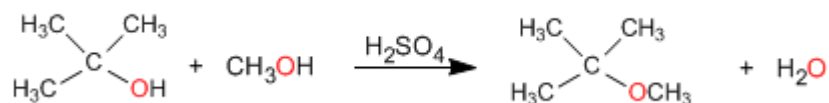


El mecanismo de la reacción transcurre en las siguientes etapas:



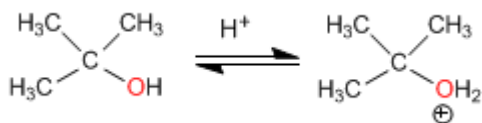
### 2. Uno de los alcoholes es secundario o terciario

En este caso la reacción transcurre en condiciones más suaves, a través de mecanismos  $\text{S}_{\text{N}}1$ .

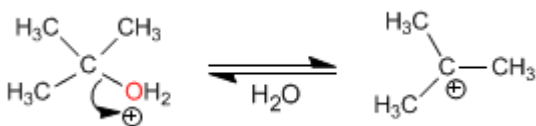


El mecanismo transcurre con formación de un carbocatión terciario de gran estabilidad

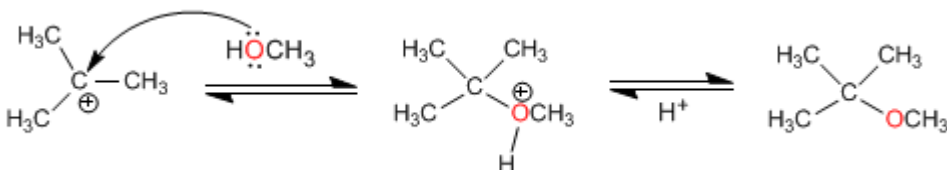
#### Etapas 1. Protonación del alcohol terciario



#### Etapas 2. Formación del carbocatión por pérdida de agua

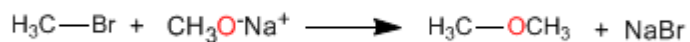


#### Etapas 3. Ataque nucleófilo del metanol



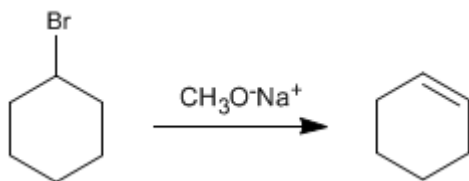
## Síntesis de Williamson de los éteres

La reacción entre un haloalcano primario y un alcóxido (o bien alcohol en medio básico) es el método más importante para preparar éteres. Esta reacción es conocida como síntesis de Williamson.

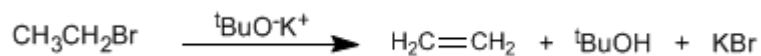


Esta reacción transcurre a través del mecanismo  $\text{S}_{\text{N}}2$ .

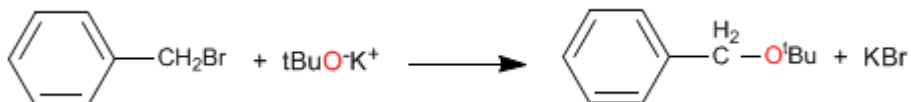
La importante basicidad de los alcóxidos produce reacciones de eliminación con sustratos secundarios y terciarios, formando alquenos en lugar de éteres.



Otra situación en la que Williamson no rinde éteres, es en el caso de emplear alcóxidos impedidos, como *tert*-butóxido de potasio. Debido a su gran tamaño el *tert*-butóxido elimina incluso con sustratos primarios.



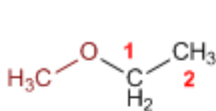
Con haloalcanos primarios y sobre todo con haloalcanos que carecen de hidrógenos β el rendimiento de Williamson es muy bueno.



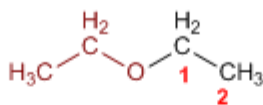
## PROBLEMAS NOMENCLATURA - ÉTERES

### Nomenclatura de Éteres - Reglas IUPAC

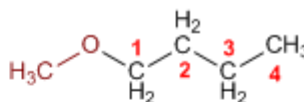
**Regla 1.** Los éteres pueden nombrarse como alcoxi derivados de alcanos (nomenclatura IUPAC sustitutiva). Se toma como cadena principal la de mayor longitud y se nombra el alcóxido como un sustituyente.



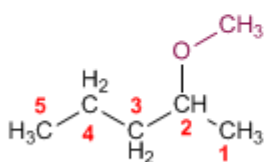
Metoxietano



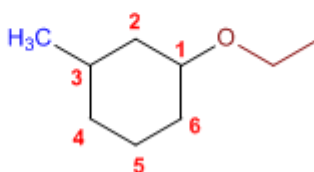
Etoxietano



1-Metoxibutano

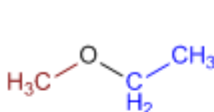


2-Metoxipentano

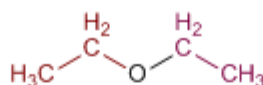


1-Etoxi-3-metilciclohexano

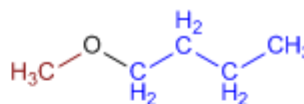
**Regla 2.** La nomenclatura funcional (IUPAC) nombra los éteres como derivados de dos grupos alquilo, ordenados alfabéticamente, terminando el nombre en la palabra éter.



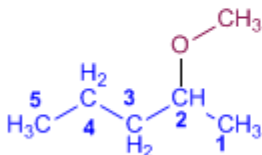
Etil metil éter



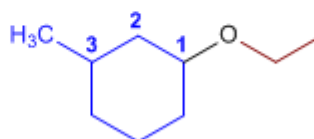
Dietil éter



Butil metil éter



Metil pent-2-il éter



Etil 3-metilciclohexil éter

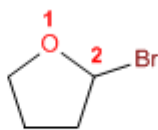
**Regla 3.** Los éteres cíclicos se forman sustituyendo un  $-\text{CH}_2-$  por  $-\text{O}-$  en un ciclo. La numeración comienza en el oxígeno y se nombran con el prefijo oxa- seguido del nombre del ciclo.



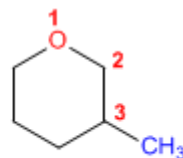
Oxaciclopropano



Oxaciclobutano



2-Bromooxaciclopentano

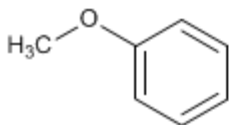


3-Metiloxaciclohexano

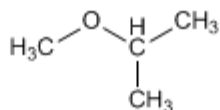
## Nomenclatura de Éteres - Problema 0.1

Nombra los siguientes éteres:

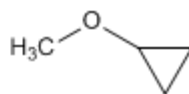
a)



b)



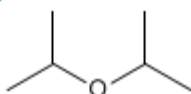
c)



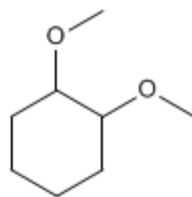
d)



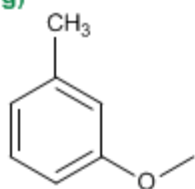
e)



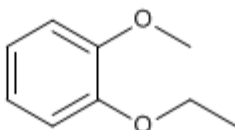
f)



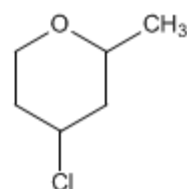
g)



h)

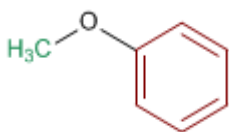


i)



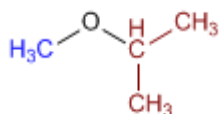
**Solución:**

a)



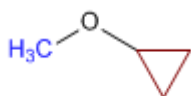
1. Sustituyentes: **fenil** y **metil**
2. Nombre: **Fenil metil** éter

b)



1. Sustituyentes: **isopropil** y **metil**
2. Nombre: **Isopropil metil** éter

c)



1. Sustituyentes: **ciclopropil** y **metil**
2. Nombre: **Ciclopropil metil** éter



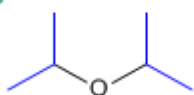
El nombre de los éteres se construye terminando en la palabra éter el nombre de las cadenas que parten del oxígeno. Estas cadenas se nombran como sustituyentes y se ordenan alfabéticamente. Obsérvese el espacio de separación entre las palabras.

d)



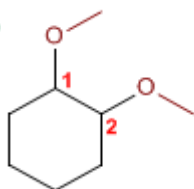
1. Sustituyentes: **etilo** y **propilo**
2. Nombre: **Etil propil** éter

e)



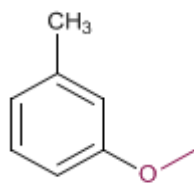
1. Sustituyentes: **isopropilos**
2. Nombre: **Diisopropil** éter

f)



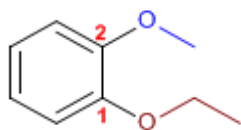
1. Cadena principal: ciclo de seis miembros (ciclohexano)
2. Numeración: otorga localizadores más bajos a sustituyentes
3. Sustituyentes: **metoxidos** en 1,2
4. Nombre: **1,2-Dimetoxiciclohexano**

g)



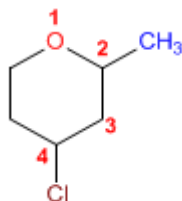
1. Cadena principal: Tolueno
2. Numeración: metilo y metóxido en meta.
3. Sustituyentes: **metoxido**
4. Nombre: **m-Metoxitolueno**

h)



1. Cadena principal: Benceno
2. Numeración: Comienza en el etoxi (antes alfabéticamente)
3. Sustituyentes: **etoxido** en 1 y **metoxido** en 2. (posición meta)
4. Nombre: **m-Etoximetoxibenceno**

i)



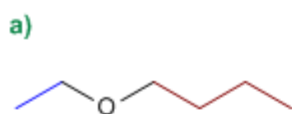
1. Cadena principal: ciclo de 6 miembros (oxaciclohexano)
2. Numeración: comienza en el oxígeno, prosigue a la derecha para otorgar a los sustituyentes los menores localizadores.
3. Sustituyentes: **cloro** y **metilo**
4. Nombre: **4-Cloro-2-metiloxaciclohexano**

## Nomenclatura de Éteres - Problema 0.2

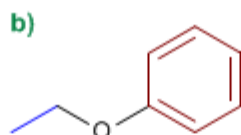
Dibuja las estructuras de los siguientes éteres:

- |                          |                                  |
|--------------------------|----------------------------------|
| a) Butil etil éter       | k) 2-Clorofenil fenil éter       |
| b) Etil fenil éter       | l) tert-butil isopropil éter     |
| c) Difenil éter          | m) 2-Metoxi-3-fenilbutan-1-ol    |
| d) Divinil éter          | n) Dietil éter                   |
| e) Isopropoxibutano      | o) m-Etoxifenol                  |
| f) Bencil fenil éter     | p) 2,3-Dimetiloxaciclopropano    |
| g) Metoxiciclohexano     | q) 3-Metoxioxaciclohexano        |
| h) 4-Metoxipent-2-eno    | r) 2-Etil-3-metiloxaciclopentano |
| i) 4-Etoxibut-1-ino      | s) Ciclohexil ciclopropil éter   |
| j) Ciclohexil fenil éter | t) 2-Metoxipentano               |

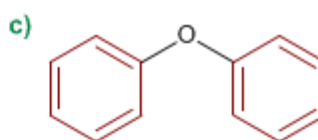
### Solución



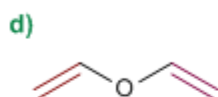
Butil etil éter



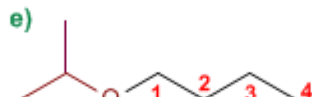
Etil fenil éter



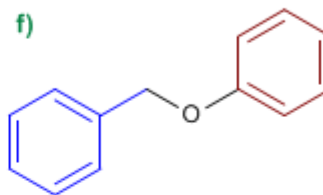
Difenil éter



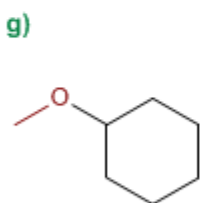
Divinil éter



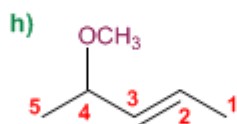
1-Isopropoxibutano



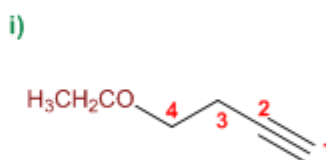
Bencil fenil éter



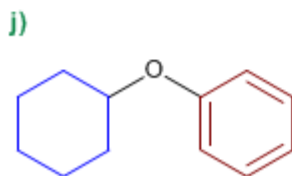
Metoxiciclohexano



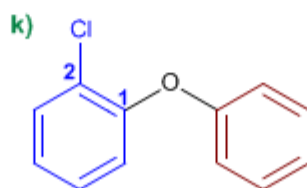
4-Metoxipent-2-eno



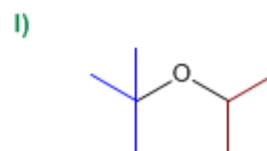
4-Etoxibut-1-ino



Ciclohexil fenil éter

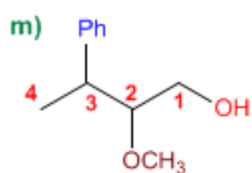


2-Clorofenil fenil éter

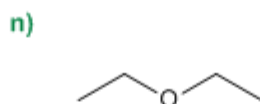


tert-butil isopropil éter

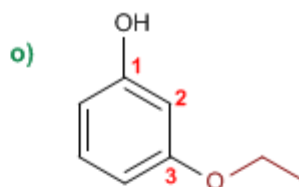
Los grupos alcóxido (metóxido, etóxido....) se ordenan alfabéticamente con los demás sustituyentes de la molécula y no tienen ninguna preferencia sobre ellos



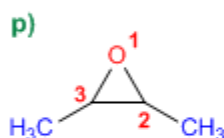
2-Metoxi-3-fenilbutan-1-ol



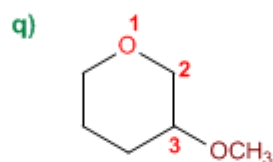
Dietil éter



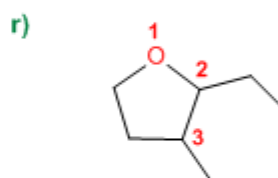
*m*-Etoxifenol



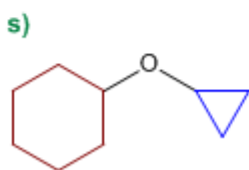
2,3-Dimetiloxa**c**ciclopropano



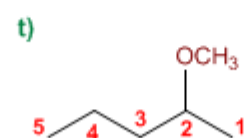
3-Metoxioxa**c**ciclohexano



2-Etil-3-metiloxa**c**ciclopentano



Ciclohexil ciclopropil éter

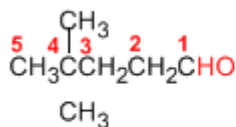


2-Metoxipentano

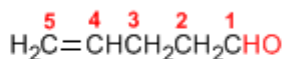
## Nomenclatura de Aldehídos y Cetonas

Los aldehídos se nombran reemplazando la terminación **-ano** del alcano correspondiente por **-al**. No es necesario especificar la posición del grupo aldehído, puesto que ocupa el extremo de la cadena (localizador 1).

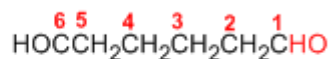
Cuando la cadena contiene dos funciones aldehído se emplea el sufijo **-dial**.



4,4-Dimetilpentanal

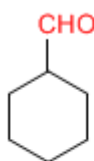


Hex-4-enal

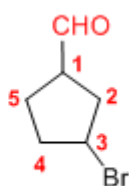


Pentanodial

El grupo **-CHO** unido a un ciclo se llama **-carbaldehído**. La numeración del ciclo se realiza dando localizador 1 al carbono del ciclo que contiene el grupo aldehído.



Ciclohexanocarbaldehído

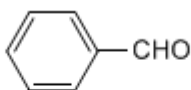


3-Bromociclopentanocarbaldehído

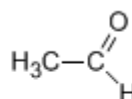
Algunos nombres comunes de aldehídos aceptados por la IUPAC son:



Formaldehído  
(Metanal)

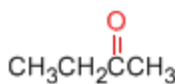


Benzaldehído  
(Bencenocarbaldehído)

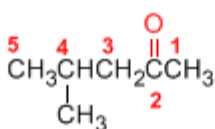


Acetaldehído  
(Etanal)

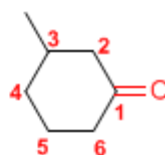
Las cetonas se nombran sustituyendo la terminación **-ano** del alcano con igual longitud de cadena por **-ona**. Se toma como cadena principal la de mayor longitud que contiene el grupo carbonilo y se numera para que éste tome el localizador más bajo.



Butanona

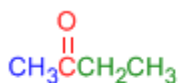


4-Metil-2-pentanona

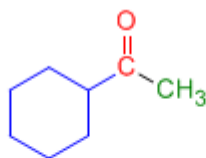


3-Metilciclohexanona

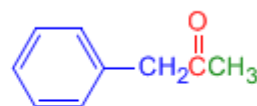
Existe un segundo tipo de nomenclatura para las cetonas, que consiste en nombrar las cadenas como sustituyentes, ordenándolas alfabéticamente y terminando el nombre con la palabra **cetona**.



Etil metil cetona



Ciclohexil metil cetona



Fenil metil cetona

[Siguiete >](#)

[\[Volver\]](#)

## Charles Friedel (1832 - 1899)



**Origen:** Químico frances..

**Lugar de nacimiento:** Estrasburgo.

**Formación:** estudió química en la Universidad de Berlín entre 1895 y 1899, consiguiendo el doctorado este año.

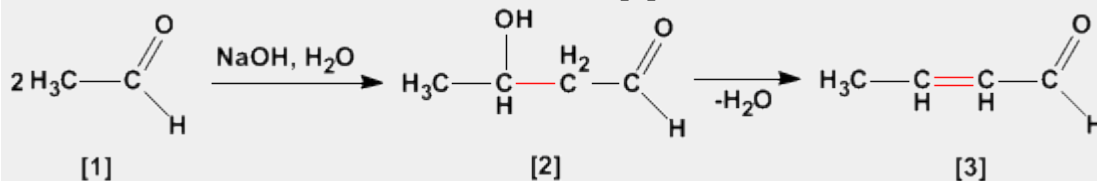
**Docencia:** Profesor en la Universidad de la Sorbona.

**Investigación:** Obtuvo el alcohol propílico. En 1877, Friedel y Crafts describieron por primera vez la reacción del benceno con un haloalcano en presencia de un ácido de Lewis. Esta reacción produce la alquilación del benceno y se conoce como alquilación de Friedl-Crafts.

**Premio Nobel:**

## Aldólica (Condensación)

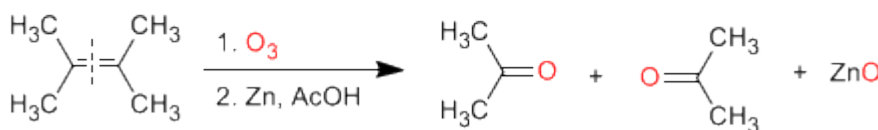
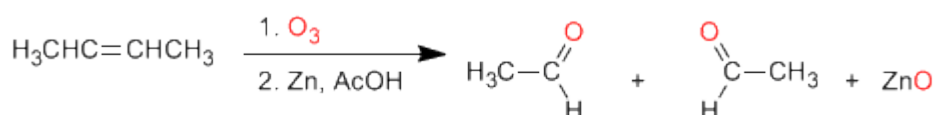
La condensación aldólica es una reacción de aldehídos o cetonas **[1]** que forma 3-hidroxicarbonilos (aldoles) **[2]**. El 3-hidroxialdehído **[2]** bajo condiciones de deshidratación por calentamiento rinde un aldehído alfa,beta-insaturado **[3]**.



## Preparación de aldehídos y cetonas

Los aldehídos y cetonas pueden ser preparados por oxidación de alcoholes, ozonólisis de alquenos, hidratación de alquinos y acilación de Friedel-Crafts como métodos de mayor importancia.

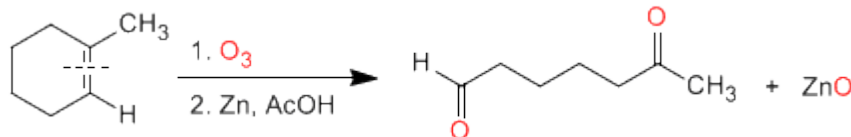
a) **Ozonólisis de alquenos:** Los alquenos rompen con ozono formando aldehídos y/o cetonas. Si el alqueno tiene hidrógenos vinílicos da aldehídos. Si tiene dos cadenas carbonadas forma cetonas.



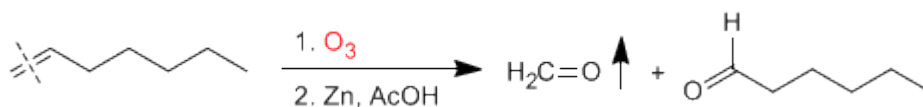
### Ozonólisis

Los alquenos simétricos y terminales permiten la preparación de carbonilos mediante ozonólisis

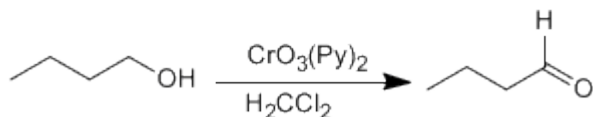
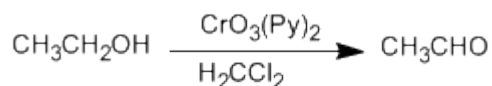
La ozonólisis de alquenos cíclicos produce compuestos dicarbonílicos:



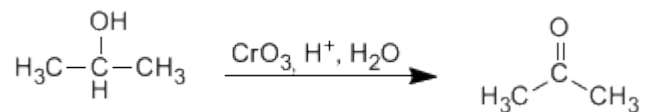
Los alquenos terminales rompen formando metanal, que separa fácilmente de la mezcla por su bajo punto de ebullición.



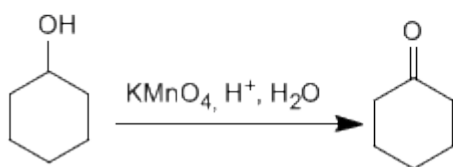
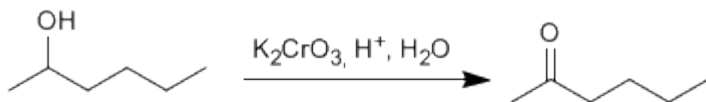
b) **Oxidación de alcoholes:** Los alcoholes primarios y secundarios se oxidan para dar aldehídos y cetonas respectivamente. Deben tomarse precauciones en la oxidación de alcoholes primarios, puesto que sobreoxidan a ácidos carboxílicos en presencia de oxidantes que contengan agua. En estos caso debe trabajarse con reactivos anhidros, como el clorocromato de piridino en diclorometano (PCC), a temperatura ambiente.



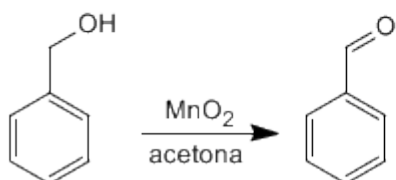
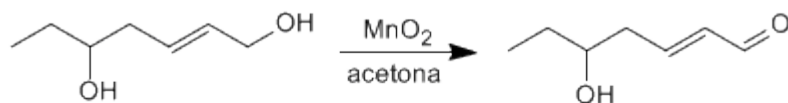
Los alcoholes secundarios dan cetonas por oxidación. Se emplean como oxidantes permanganato, dicromato, trióxido de cromo.



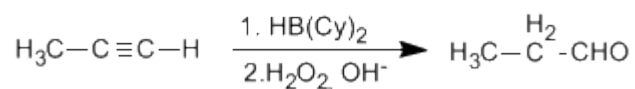
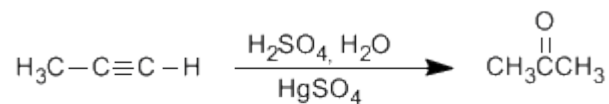
La oxidación supone la pérdida de dos hidrógenos del alcohol. Los alcoholes terciarios no pueden oxidar puesto que carecen de hidrógeno sobre el carbono.



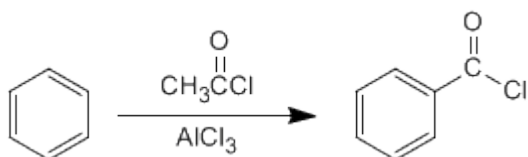
Los alcoholes alílicos y bencílicos se transforman en aldehídos o cetonas por oxidación con dióxido de manganeso en acetona. Esta reacción tiene una elevada selectividad y no oxida alcoholes que no se encuentren en dichas posiciones.



c) **Hidratación de alquinos:** Los alquinos se pueden hidratar Markovnikov, formando cetonas, o bien antiMarkovnikov, para formar aldehídos.



d) **Acilación de Friedel-Crafts:** La introducción de grupos acilo en el benceno permite la preparación de cetonas con cadenas aromáticas.



### Otto Paul Hermann Diels (1876 - 1954)



**Origen:** Químico alemán.

**Lugar de nacimiento:** Königshütte (hoy Chorzów, Polonia).

**Formación:** estudió química en la Universidad de Berlín entre 1895 y 1899, consiguiendo el doctorado este año.

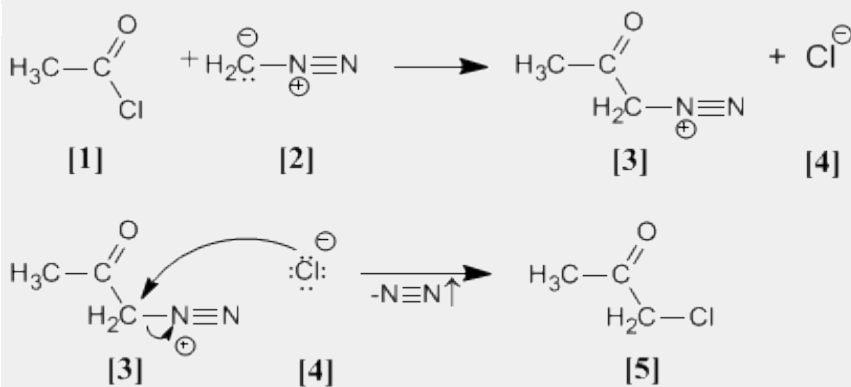
**Docencia:** profesor y jefe del departamento de química en la Universidad de Berlín. En 1916, tomó el puesto de profesor de Química en la Universidad de Kiel, cargo que no dejó hasta su jubilación en 1945.

**Investigación:** En 1906 descubrió el anhídrido malónico. Investigó en reacciones de deshidrogenación con selenio. Síntesis de  $\alpha$ -dicetonas. Pero su trabajo más importante es la reacción de Diels - Alder.

**Premio Nobel:** En 1950 recibió el Premio Nobel junto a Kurt Alder

### Arndt Eistert (Síntesis)

Cloruro de acetilo [1] se trata con diazometano [2] rindiendo la sal de diazonio [3]. El cloruro [4] producido reacciona con la sal de diazonio para dar la  $\alpha$ -clorocetona [5].



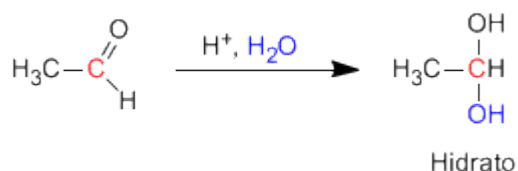
#### Síntesis de Arndt Eistert

Esta reacción permite transformar haluros de alcanoilo en cetonas halogenadas en su posición alfa.



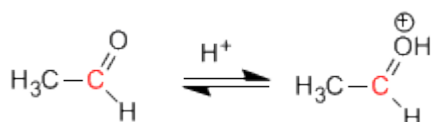
## Formación de Hidratos

Los aldehídos y cetonas reaccionan en medio ácido acuoso para formar hidratos. El mecanismo consta de tres etapas. La primera y más rápida consiste en la protonación del oxígeno carbonílico. Esta protonación produce un aumento de la polaridad sobre el carbono y favorece el ataque del nucleófilo. En la segunda etapa el agua ataca al carbono carbonilo, es la etapa lenta del mecanismo. En la tercera etapa se produce la desprotonación del oxígeno formándose el hidrato final.

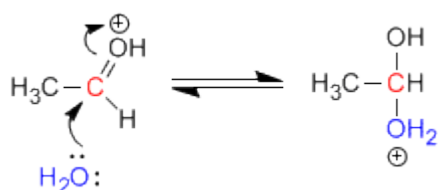


### Mecanismo de la reacción

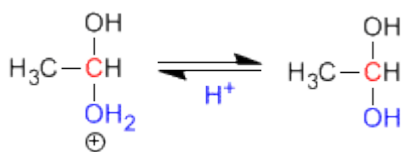
Etapa 1. Protonación del oxígeno carbonílico.



Etapa 2. Ataque nucleófilo del agua al carbonilo protonado.



Etapa 3. Desprotonación del hidrato





**Origen:** Químico estadounidense.

**Lugar de nacimiento:** Budapest

**Formación:** Se doctoró en la Universidad de Budapest en 1949

**Docencia:** Trabajó en el departamento de química orgánica de la Academia de Ciencias de Hungría y posteriormente en la Universidad de Cleveland.

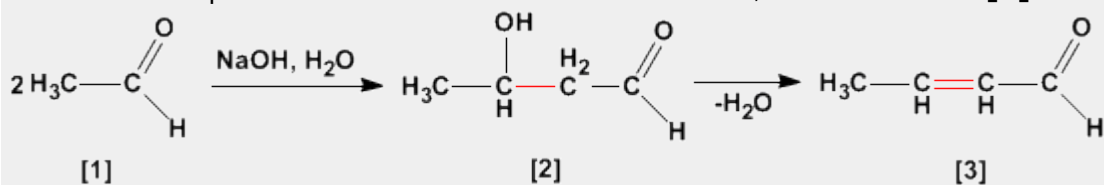
**Industria:** Trabajó en los laboratorios de la Dow Chemical de Ontario

**Investigación:** Olah consiguió preparar carbocationes estables utilizando componentes extremadamente ácidos.

**Premio Nobel:** En 1994 obtuvo el premio Nobel de Química por sus investigaciones sobre los carbocationes

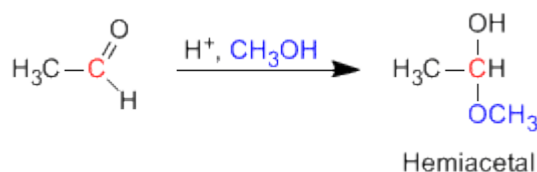
### Aldólica (Condensación)

La condensación aldólica es una reacción de aldehídos o cetonas **[1]** que forma 3-hidroxicarbonilos (aldoles) **[2]**. El 3-hidroxialdehído **[2]** bajo condiciones de deshidratación por calentamiento rinde un aldehído alfa,beta-insaturado **[3]**.



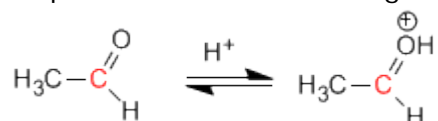
## Formación de Hemiacetales

Los hemiacetales se forman por reacción de un equivalente de alcohol con el grupo carbonilo de un aldehído o cetona. Esta reacción se cataliza con ácido y es equivalente a la formación de hidratos.

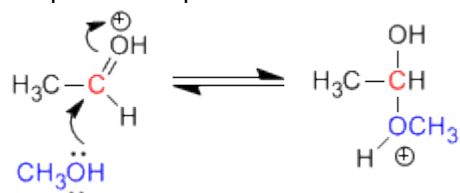


### Mecanismo de la reacción:

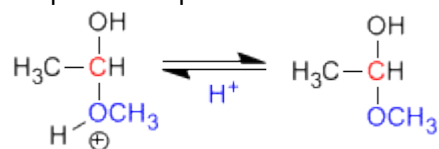
Eta 1. Protonación del oxígeno carbonílico.



Eta 2. Ataque nucleófilo del metanol al carbonilo protonado.



Eta 3. Desprotonación del hemiacetal



## Otto Paul Hermann Diels (1876 - 1954)



**Origen:** Químico alemán.

**Lugar de nacimiento:** Königshütte (hoy Chorzów, Polonia).

**Formación:** estudió química en la Universidad de Berlín entre 1895 y 1899, consiguiendo el doctorado este año.

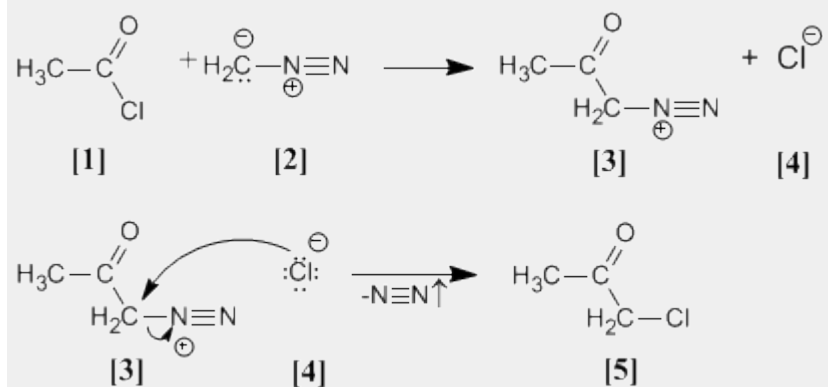
**Docencia:** profesor y jefe del departamento de química en la Universidad de Berlín. En 1916, tomó el puesto de profesor de Química en la Universidad de Kiel, cargo que no dejó hasta su jubilación en 1945.

**Investigación:** En 1906 descubrió el anhídrido malónico. Investigó en reacciones de deshidrogenación con selenio. Síntesis de  $\alpha$ -dicetonas. Pero su trabajo más importante es la reacción de Diels - Alder.

**Premio Nobel:** En 1950 recibió el Premio Nobel junto a Kurt Alder

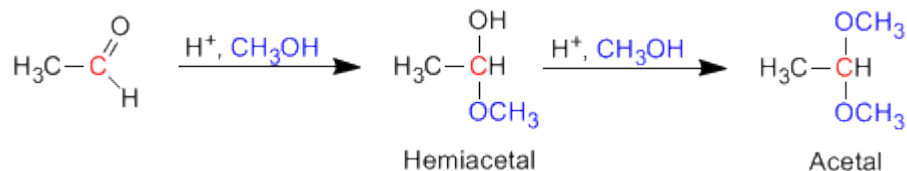
### Arndt Eistert (Síntesis)

Cloruro de acetilo **[1]** se trata con diazometano **[2]** rindiendo la sal de diazonio **[3]**. El cloruro **[4]** producido reacciona con la sal de diazonio para dar la  $\alpha$ -clorocetona **[5]**.



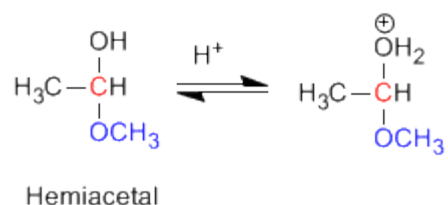
## Formación de Acetales

Los aldehídos y cetonas reaccionan con alcoholes bajo condiciones de catálisis ácida, formando en una primera etapa hemiacetales, que posteriormente evolucionan por reacción con un segundo equivalente de alcohol a acetales.

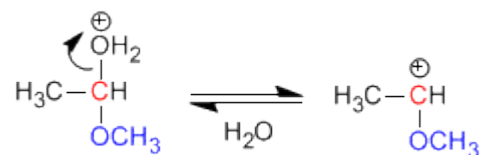


### Mecanismo para la formación de acetales

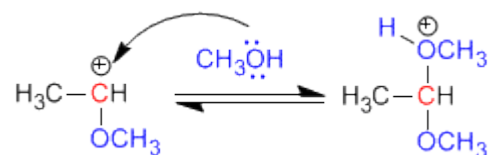
Etapa 1. Protonación del grupo hidroxilo



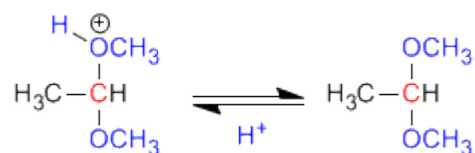
Etapa 2. Pérdida de agua.



Etapa 3. Ataque del alcohol al carbocatión



Etapa 4. Desprotonación del acetal



### Otto Paul Hermann Diels (1876 - 1954)



**Origen:** Químico alemán.

**Lugar de nacimiento:** Königshütte (hoy Chorzów, Polonia).

**Formación:** estudió química en la Universidad de Berlín entre 1895 y 1899, consiguiendo el doctorado este año.

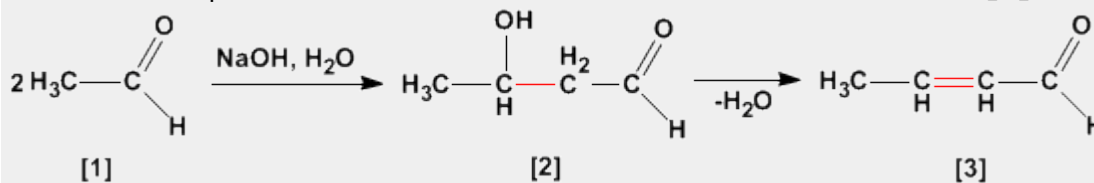
**Docencia:** profesor y jefe del departamento de química en la Universidad de Berlín. En 1916, tomó el puesto de profesor de Química en la Universidad de Kiel, cargo que no dejó hasta su jubilación en 1945.

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**Premio Nobel:** En 1950 recibió el Premio Nobel junto a Kurt Alder

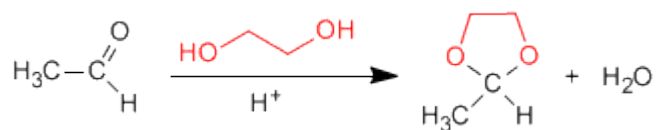
### Aldólica (Condensación)

La condensación aldólica es una reacción de aldehídos o cetonas **[1]** que forma 3-hidroxicarbonilos (aldoles) **[2]**. El 3-hidroxialdehído **[2]** bajo condiciones de deshidratación por calentamiento rinde un aldehído alfa,beta-insaturado **[3]**.



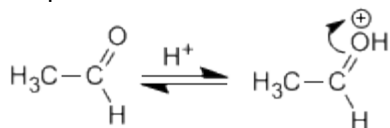
## Formación de acetales cíclicos

Los 1,2- y 1,3-dioles reaccionan con aldehídos y cetonas formando acetales cíclicos. Los equilibrios se desplazan hacia el producto final eliminando el agua formada por destilación azeotrópica con benceno o tolueno.

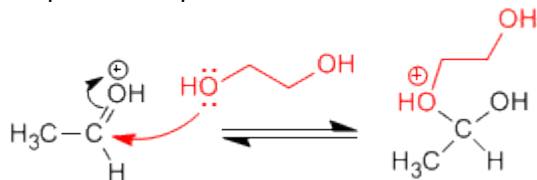


### Mecanismo para la formación de acetales cíclicos:

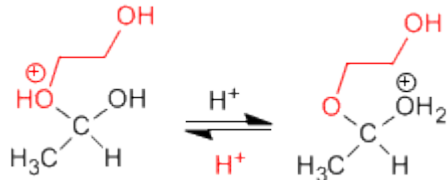
Etapa 1. Protonación del carbonilo



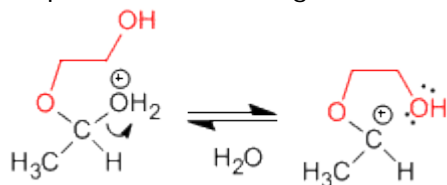
Etapa 2. Ataque nucleófilo del diol al carbonilo.



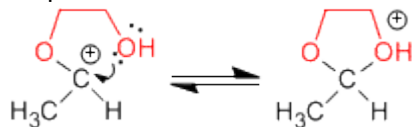
Etapa 3. Equilibrio ácido base entre el éter y el alcohol



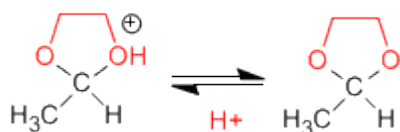
Etapa 4. Pérdida de agua



Etapa 5. Ciclación



Etapa 6. Desprotonación del acetal cíclico



### Kurt Alder (1902 - 1958)



**Origen:** Químico alemán.

**Lugar de nacimiento:** Königshütte (hoy Chorzów, Polonia).

**Formación:** estudió en la Universidad de Kiel. Bajo la supervisión del químico alemán Otto Diels, su jefe e instructor en Kiel.

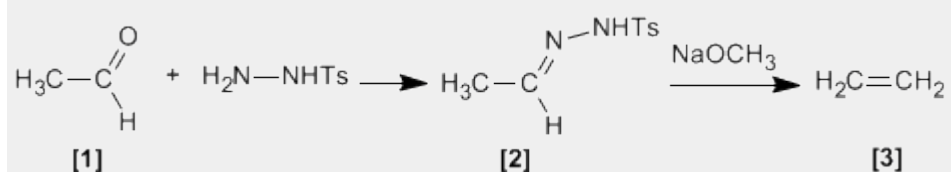
**Docencia:** Alder ejerció como profesor de química en las universidades de Kiel y Colonia.

**Investigación:** Alder se especializó en la síntesis diénica (conocida más tarde como la reacción Diels - Alder) que consiste fundamentalmente en el análisis y formación de compuestos orgánicos complejos. Ya en 1928 ambos fueron coautores de un ensayo sobre este proceso.

**Premio Nobel:** En 1950 recibió el Premio Nobel junto a Diels

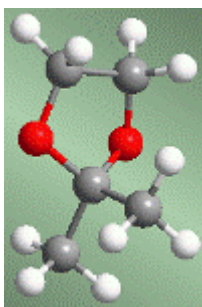
### Bamford Stevens (Reacción)

Tosilhidrazonas [2] de aldehídos o cetonas alifáticos [1] reaccionan con bases fuertes para dar alquenos [3].



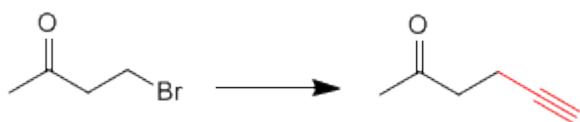


## Acetales como grupos protectores

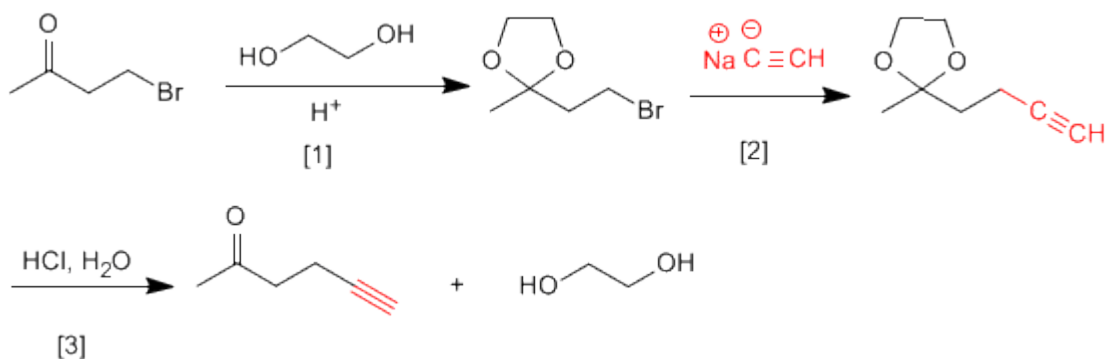


Los acetales pueden emplearse, por su estabilidad, como grupos protectores del carbonilo. El acetal es un éter, muy estable en medios básicos, aunque rompe en presencia de medios ácidos. En muchos procesos de síntesis el grupo carbonilo es incompatible con el reactivo utilizado. En estos casos debe protegerse para evitar que reaccione. La inestabilidad del acetal en medio ácido puede emplearse para desproteger el carbonilo.

Veamos algunos ejemplos:



Esta transformación requiere una sustitución, empleando como nucleófilo un acetiluro de sodio. El nucleófilo puede atacar también al grupo carbonilo, para evitarlo vamos a protegerlo.

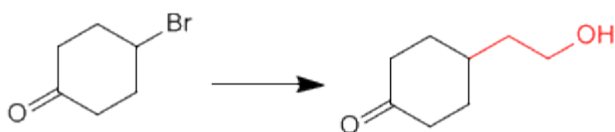


[1] Protección de la cetona.

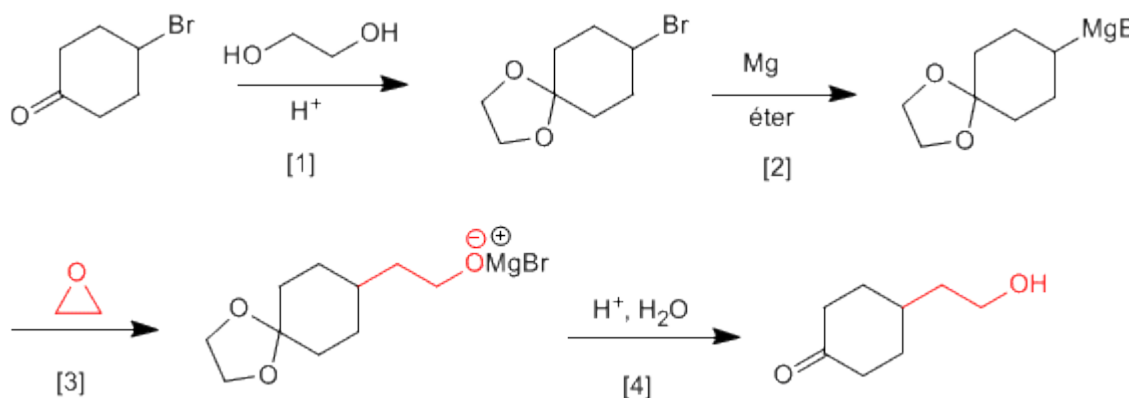
[2] Ataque del acetiluro al carbono del bromo.

[3] Desprotección del carbonilo

Veamos un segundo ejemplo:



Es necesario proteger la cetona antes de formar el organometálico para evitar la dimerización del compuesto.



- [1] Protección de la cetona.  
 [2] Formación del magnesiano.  
 [3] Apertura del oxaciclopropano.  
 [4] Desprotección y protonación del alcóxido.

### Otto Paul Hermann Diels (1876 - 1954)



**Origen:** Químico alemán.

**Lugar de nacimiento:** Königshütte (hoy Chorzów, Polonia).

**Formación:** estudió química en la Universidad de Berlín entre 1895 y 1899, consiguiendo el doctorado este año.

**Docencia:** profesor y jefe del departamento de química en la Universidad de Berlín. En 1916, tomó el puesto de profesor de Química en la Universidad de Kiel, cargo que no dejó hasta su jubilación en 1945.

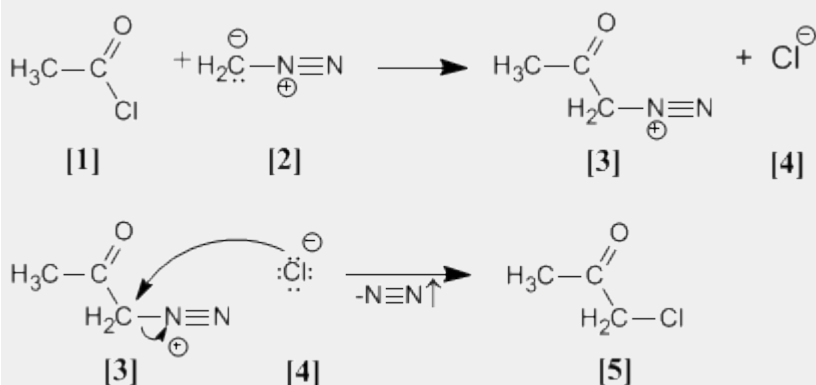
**Investigación:** En 1906 descubrió el anhídrido malónico.

Investigó en reacciones de deshidrogenación con selenio. Síntesis de  $\alpha$ -dicetonas. Pero su trabajo más importante es la reacción de Diels - Alder.

**Premio Nobel:** En 1950 recibió el Premio Nobel junto a Kurt Alder

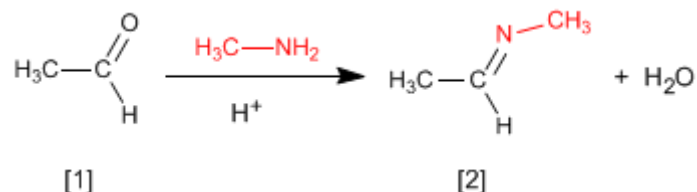
### Arndt Eistert (Síntesis)

Cloruro de acetilo [1] se trata con diazometano [2] rindiendo la sal de diazonio [3]. El cloruro [4] producido reacciona con la sal de diazonio para dar la  $\alpha$ -clorocetona [5].



## Formación de Iminas

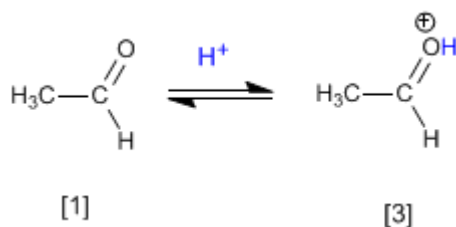
La reacción de aldehídos o cetonas **[1]** con aminas primarias genera iminas **[2]**. La reacción se favorece en un medio ligeramente ácido (pH=4.5).



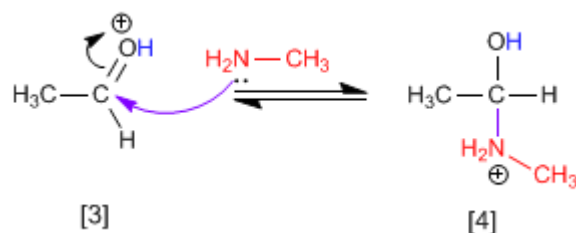
El control del pH es fundamental, puesto que se requiere la protonación del oxígeno del carbonilo para favorecer el ataque nucleófilo.

### Mecanismo:

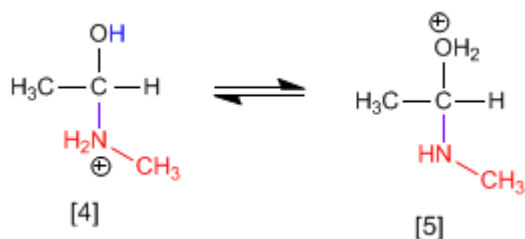
**Etapas 1.** Protonación del grupo carbonilo que aumenta la polaridad positiva sobre el carbono y favorece el ataque nucleófilo.



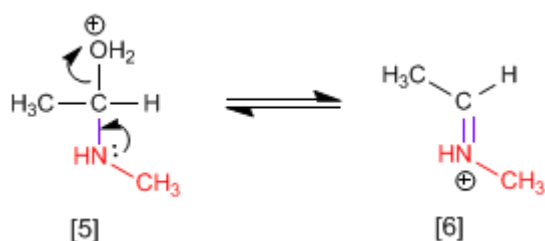
**Etapas 2.** Ataque nucleófilo de la amina primaria al carbono carbonilo.



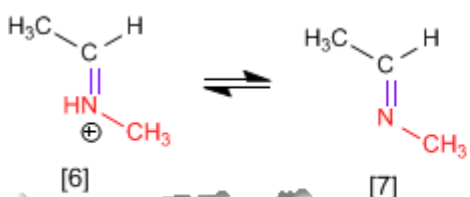
**Etapas 3.** Protonación del grupo hidroxilo para transformarlo en buen grupo saliente.



**Etapas 4.** Pérdida de agua y formación de la imina protonada.



### Etapa 5. Desprotonación del catión.



### George A. Olah (1927 - )



**Origen:** Químico estadounidense.

**Lugar de nacimiento:** Budapest

**Formación:** Se doctoró en la Universidad de Budapest en 1949

**Docencia:** Trabajó en el departamento de química orgánica de la Academia de Ciencias de Hungría y posteriormente en la Universidad de Cleveland.

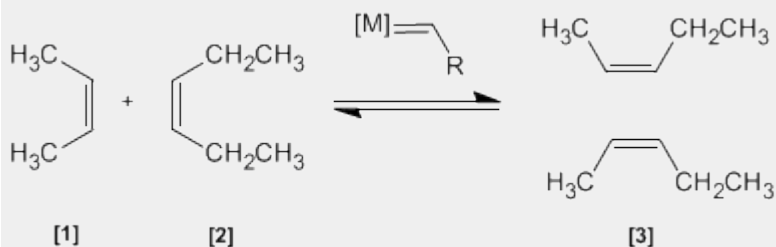
**Industria:** Trabajó en los laboratorios de la Dow Chemical de Ontario

**Investigación:** Olah consiguió preparar carbocationes estables utilizando componentes extremadamente ácidos.

**Premio Nobel:** En 1994 obtuvo el premio Nobel de Química por sus investigaciones sobre los carbocationes

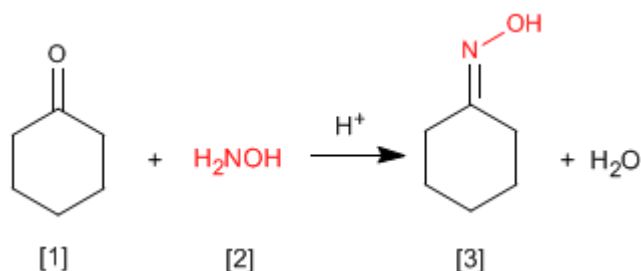
### Metátesis de Alquenos

En esta reacción dos alquenos **[1]** y **[2]** son tratados con un metal de transición que actúa como catalizador, dando una mezcla de alquenos **[3]** (incluyendo isómeros Z/E). Este productos se obtiene por intercambio de grupos alquilideno.

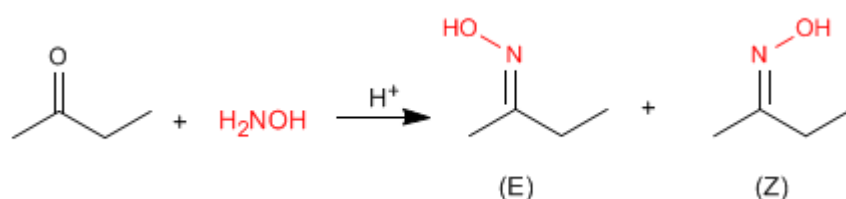


## Formación de Oximas

Las oximas [3] se obtienen por reacción de aldehídos o cetonas [1] e hidroxilamina [2] en un medio débilmente ácido. El mecanismo es análogo al de formación de iminas.



Las oximas de aldehídos y cetona asimétricas presentan isomería Z/E dependiendo de la posición del hidroxilo.



Las iminas e hidrazonas (que comentaremos a continuación) también presentan esta característica.

### George A. Olah (1927 - )



**Origen:** Químico estadounidense.

**Lugar de nacimiento:** Budapest

**Formación:** Se doctoró en la Universidad de Budapest en 1949

**Docencia:** Trabajó en el departamento de química orgánica de la Academia de Ciencias de Hungría y posteriormente en la Universidad de Cleveland.

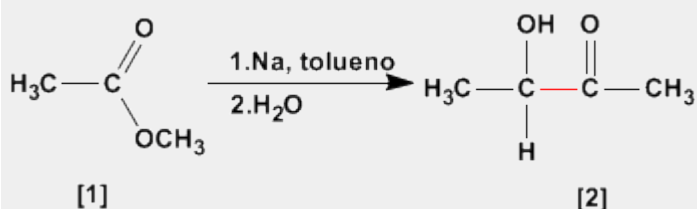
**Industria:** Trabajó en los laboratorios de la Dow Chemical de Ontario

**Investigación:** Olah consiguió preparar carbocationes estables utilizando componentes extremadamente ácidos.

**Premio Nobel:** En 1994 obtuvo el premio Nobel de Química por sus investigaciones sobre los carbocationes

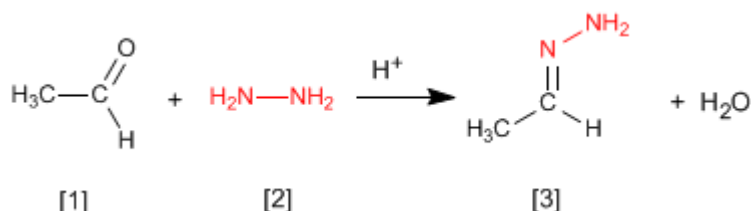
## Aciloinica (Condensación)

La condensación aciloinica transforma ésteres [1] en alfa-hidroxicetonas [2]. Esta reacción se realiza con sodio metal en disolvente inerte.

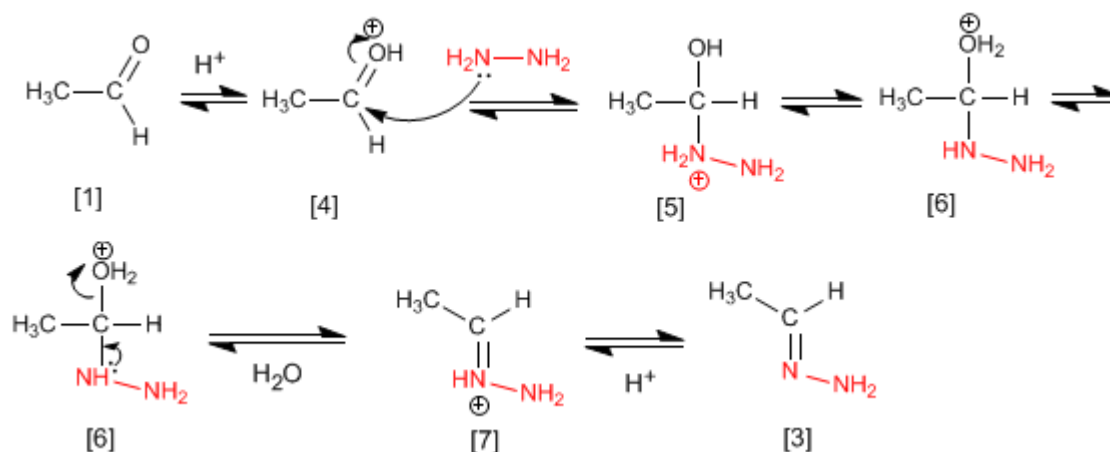


## Formación de Hidrazonas

Las hidrazonas [3] se obtienen por reacción de aldehídos o cetonas [1] con hidrazina [2]. Igual que en el caso de las iminas y oximas requiere pH=4.



Aunque el mecanismo es análogo al de formación de iminas, comentaremos de nuevo los pasos.



El etanal [1] se protona formando su ácido conjugado [4]. La importante polaridad del carbono carbonilo de [4] favorece el ataque de la hidrazina [2] para formando el intermedio [5]. El compuesto [5] intercambia un protón entre el nitrógeno y el oxígeno, transformando el grupo hidroxilo en agua (buen grupo saliente). El intermedio [6] pierde una molécula de agua transformándose en [7], cuya desprotonación da la hidrazona final [3].

### Kurt Alder (1902 - 1958)



**Origen:** Químico alemán.

**Lugar de nacimiento:** Königshütte (hoy Chorzów, Polonia).

**Formación:** estudió en la Universidad de Kiel. Bajo la supervisión del químico alemán Otto Diels, su jefe e instructor en Kiel.

**Docencia:** Alder ejerció como profesor de química en las universidades de Kiel y Colonia.

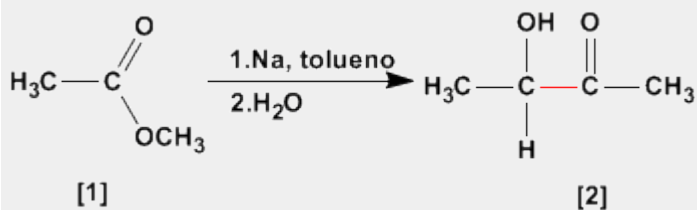
**Investigación:** Alder se especializó en la síntesis diénica (conocida más tarde como la reacción Diels - Alder) que consiste fundamentalmente en el análisis y formación de compuestos orgánicos complejos.

Ya en 1928 ambos fueron coautores de un ensayo sobre este proceso.

**Premio Nobel:** En 1950 recibió el Premio Nobel junto a Diels

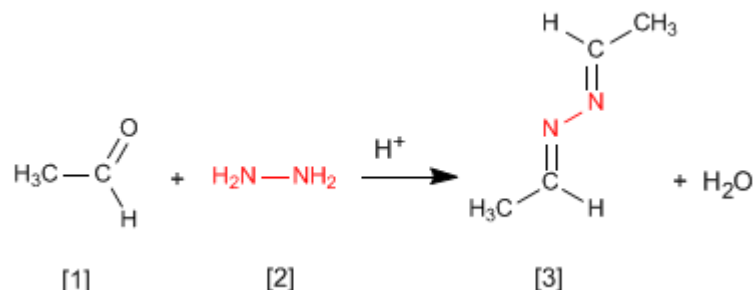
### Aciloínica (Condensación)

La condensación aciloínica transforma esteres [1] en alfa-hidroxicetonas [2]. Esta reacción se realiza con sodio metal en disolvente inerte.



## Formación de Azinas

La hidrazina [2] reacciona con dos moléculas de aldehído [1] para formar azinas [3].



El mecanismo es análogo al de formación de iminas, oximas e hidrazonas.

### George A. Olah (1927 - )



**Origen:** Químico estadounidense.

**Lugar de nacimiento:** Budapest

**Formación:** Se doctoró en la Universidad de Budapest en 1949

**Docencia:** Trabajó en el departamento de química orgánica de la Academia de Ciencias de Hungría y posteriormente en la

Universidad de Cleveland.

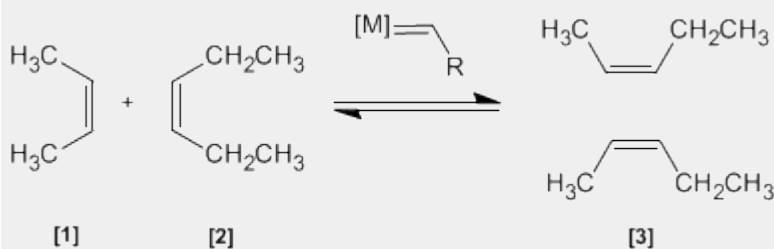
**Industria:** Trabajó en los laboratorios de la Dow Chemical de Ontario

**Investigación:** Olah consiguió preparar carbocationes estables utilizando componentes extremadamente ácidos.

**Premio Nobel:** En 1994 obtuvo el premio Nobel de Química por sus investigaciones sobre los carbocationes

## Metátesis de Alquenos

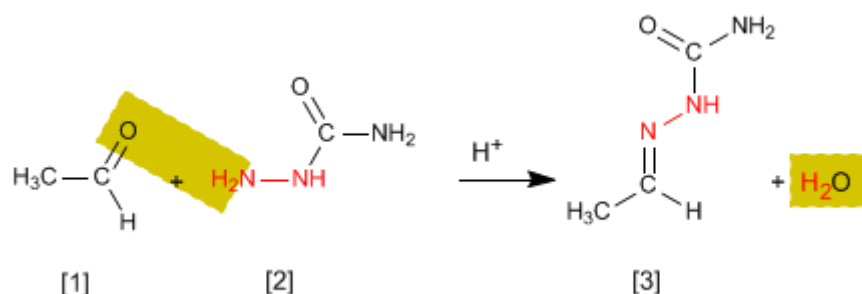
En esta reacción dos alquenos [1] y [2] son tratados con un metal de transición que actúa como catalizador, dando una mezcla de alquenos [3] (incluyendo isómeros Z/E). Este producto se obtiene por intercambio de grupos alquilideno.





## Formación de Semicarbazonas

Las semicarbazonas [3] se obtienen por reacción de aldehídos o cetonas [1] con semicarbazida [2]. Veamos un ejemplo:



El mecanismo es análogo al de formación de iminas, oximas e hidrazonas.

### Charles Friedel (1832 - 1899)



**Origen:** Químico frances..

**Lugar de nacimiento:** Estrasburgo.

**Formación:** estudió química en la Universidad de Berlín entre 1895 y 1899, consiguiendo el doctorado este año.

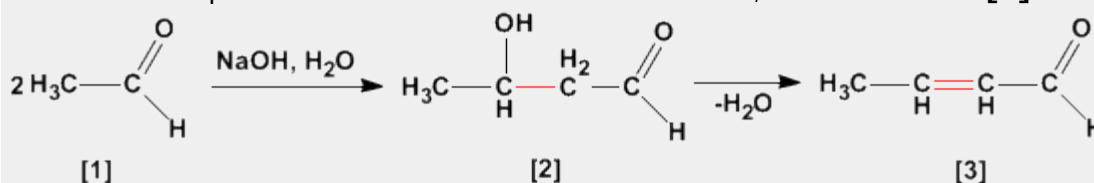
**Docencia:** Profesor en la Universidad de la Sorbona.

**Investigación:** Obtuvo el alcohol propílico. En 1877, Friedel y Crafts describieron por primera vez la reacción del benceno con un haloalcano en presencia de un ácido de Lewis. Esta reacción produce la alquilación del benceno y se conoce como alquilación de Friedl-Crafts.

**Premio Nobel:**

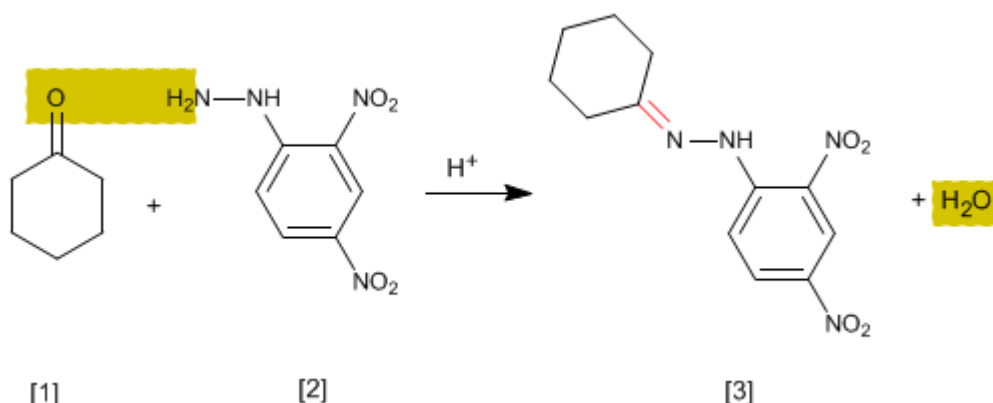
### Aldólica (Condensación)

La condensación aldólica es una reacción de aldehídos o cetonas [1] que forma 3-hidroxicarbonilos (aldoles) [2]. El 3-hidroxialdehído [2] bajo condiciones de deshidratación por calentamiento rinde un aldehído alfa,beta-insaturado [3].



## Ensayo de la 2,4-Dinitrofenilhidrazina

Se trata de un ensayo analítico específico de aldehídos y cetonas. Los carbonilos **[1]** reaccionan con 2,4-Dinitrofenilhidrazina **[2]** formando fenilhidrazonas **[3]** que precipitan de color amarillo. La aparición de precipitado es un indicador de la presencia de carbonilos en el medio.



El mecanismo de la reacción es análogo al de formación de iminas.

### Kurt Alder (1902 - 1958)



**Origen:** Químico alemán.

**Lugar de nacimiento:** Königshütte (hoy Chorzów, Polonia).

**Formación:** estudió en la Universidad de Kiel. Bajo la supervisión del químico alemán Otto Diels, su jefe e instructor en Kiel.

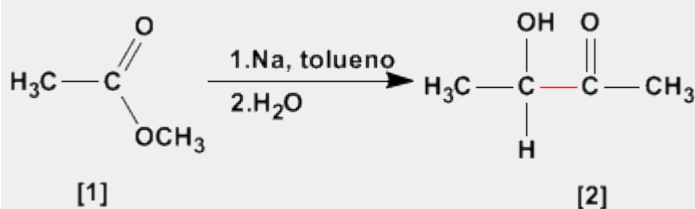
**Docencia:** Alder ejerció como profesor de química en las universidades de Kiel y Colonia.

**Investigación:** Alder se especializó en la síntesis diénica (conocida más tarde como la reacción Diels - Alder) que consiste fundamentalmente en el análisis y formación de compuestos orgánicos complejos. Ya en 1928 ambos fueron coautores de un ensayo sobre este proceso.

**Premio Nobel:** En 1950 recibió el Premio Nobel junto a Diels

### Aciloinica (Condensación)

La condensación aciloinica transforma esteres **[1]** en alfa-hidroxicetonas **[2]**. Esta reacción se realiza con sodio metal en disolvente inerte.



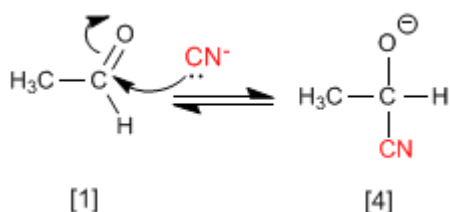
## Formación de Cianhidrinas

Las cianhidrinas **[3]** se forman por reacción de aldehídos o cetonas **[1]** con ácido cianhídrico **[2]** y son compuestos que contienen un grupo ciano y un hidroxilo sobre el mismo carbono.

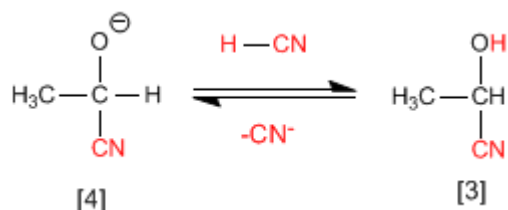


El mecanismo de la reacción transcurre en dos etapas:

**Etapla 1.** Los iones cianuro actúan como nucleófilos atacando al carbono carbonilo. El ácido cianhídrico es demasiado débil para generar cantidades importantes de cianuro, por ello, se añade cianuro de sodio o potasio al medio, garantizando la cantidad suficiente de cianuro para que la reacción transcurra en buen rendimiento.



**Etapla 2.** En este paso el ión alcóxido **[4]** se protona arrancando hidrógenos al ácido cianhídrico. En esta etapa se regeneran los iones cianuro.



### Kurt Alder (1902 - 1958)



**Origen:** Químico alemán.

**Lugar de nacimiento:** Königshütte (hoy Chorzów, Polonia).

**Formación:** estudió en la Universidad de Kiel. Bajo la supervisión del químico alemán Otto Diels, su jefe e instructor en Kiel.

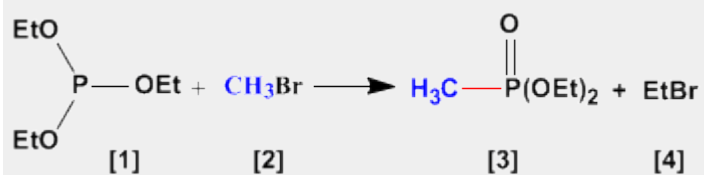
**Docencia:** Alder ejerció como profesor de química en las universidades de Kiel y Colonia.

**Investigación:** Alder se especializó en la síntesis diénica (conocida más tarde como la reacción Diels - Alder) que consiste fundamentalmente en el análisis y formación de compuestos orgánicos complejos. Ya en 1928 ambos fueron coautores de un ensayo sobre este proceso.

**Premio Nobel:** En 1950 recibió el Premio Nobel junto a Diels

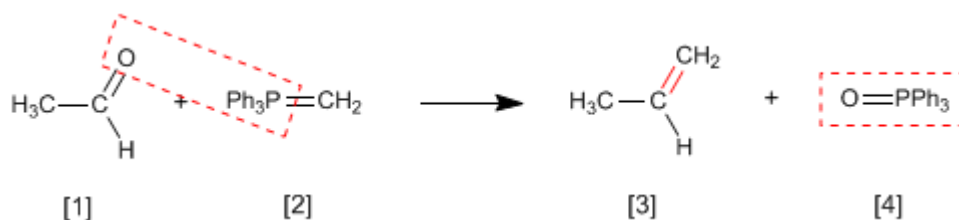
### Arbuzov (Reacción)

La reacción de Arbuzov se emplea en la síntesis de fosfonatos **[3]** a partir de fosfitos **[1]**. Los fosfonatos obtenidos en la síntesis de Arbuzov se emplean como materiales de partida en la síntesis de Horner-Wittig.



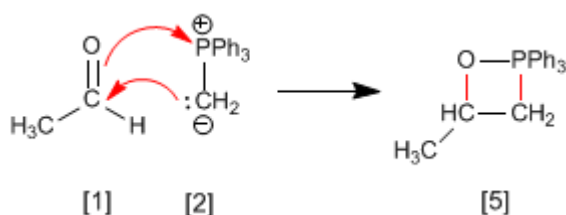
## Reacción de Wittig

La reacción de Wittig emplea iluros de fósforo [2] para transformar aldehídos y cetonas [1] en alquenos [3]. Como subproducto se obtiene el óxido de trifenilfosfina [4].

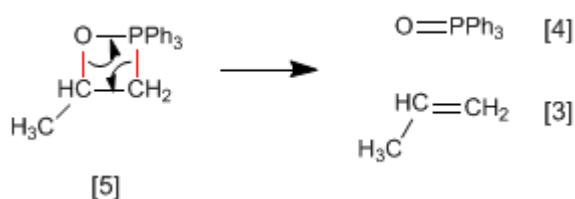


En el mecanismo de la reacción el iluro y el carbonilo se combinan para formar un oxafosfetano que rompe dejando libre el alqueno final.

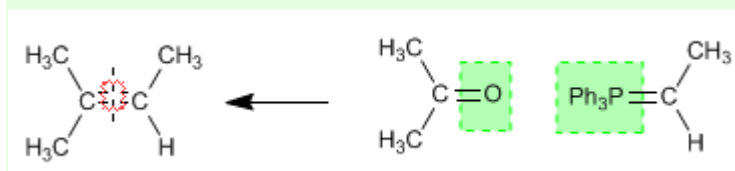
**Etapas 1.** El etanal y el iluro se combinan formando el fosfetano.



**Etapas 2.** El fosfetano rompe formando el alqueno y óxido de trifenilfosfina.

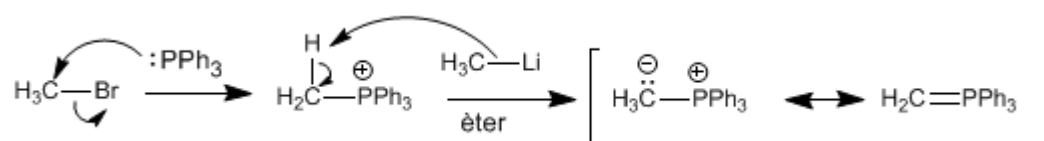


Ejemplo - Obtener mediante Wittig el 2-Metilbut-2-eno



Se rompe el alqueno por el doble enlace y a cada carbono se le agrega el grupo encerrado en verde.

Los **iluros de fósforo** se preparan mediante reacción de haloalcanos y trifenilfosfina, seguido de desprotonación del carbono con base fuerte (organometálicos de litio).



### Charles Friedel (1832 - 1899)



**Origen:** Químico frances..

**Lugar de nacimiento:** Estrasburgo.

**Formación:** estudió química en la Universidad de Berlín entre 1895 y 1899, consiguiendo el doctorado este año.

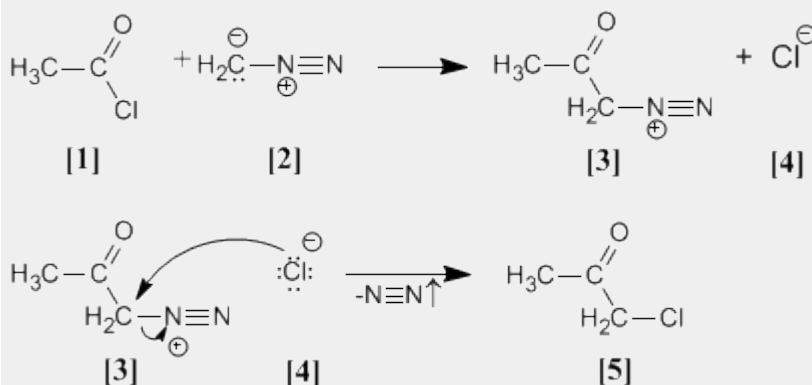
**Docencia:** Profesor en la Universidad de la Sorbona.

**Investigación:** Obtuvo el alcohol propílico. En 1877, Friedel y Crafts describieron por primera vez la reacción del benceno con un haloalcano en presencia de un ácido de Lewis. Esta reacción produce la alquilación del benceno y se conoce como alquilación de Friedl-Crafts.

**Premio Nobel:**

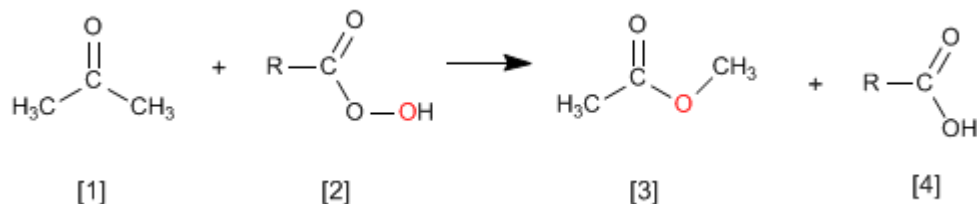
### Arndt Eistert (Síntesis)

Cloruro de acetilo **[1]** se trata con diazometano **[2]** rindiendo la sal de diazonio **[3]**. El cloruro **[4]** producido reacciona con la sal de diazonio para dar la α-clorocetona **[5]**.

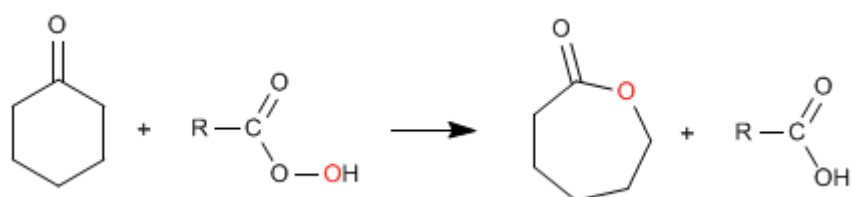


## Oxidación de Baeyer Villiger

La reacción de cetonas **[1]** con perácidos **[2]** produce ésteres **[3]**. El oxígeno del perácido se inserta entre el carbono carbonilo y el carbono alfa de la cetona. Esta reacción fue descrita por Adolf von Baeyer y Victor Villiger in 1899.

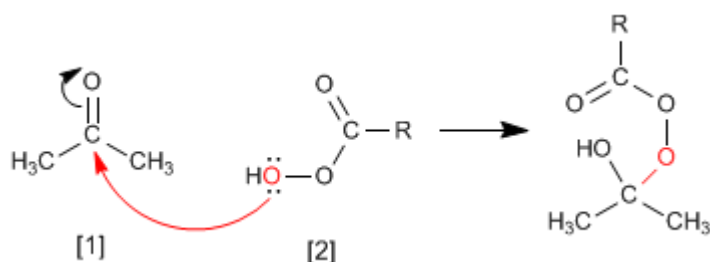


A partir de cetonas cíclicas se obtienen ésteres cíclicos (lactonas)

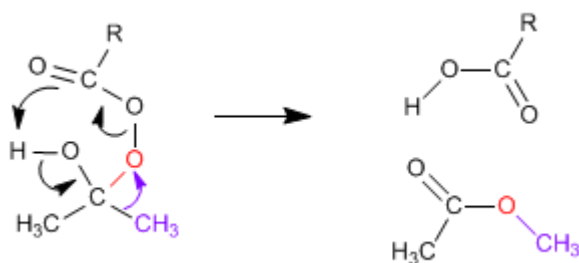


El mecanismo de Baeyer Villiger comienza con el ataque nucleófilo del perácido sobre el carbonilo, seguido de la migración del sustituyente desde el grupo carbonilo al oxígeno del perácido.

**Etapas 1.** Adición del perácido al carbonilo

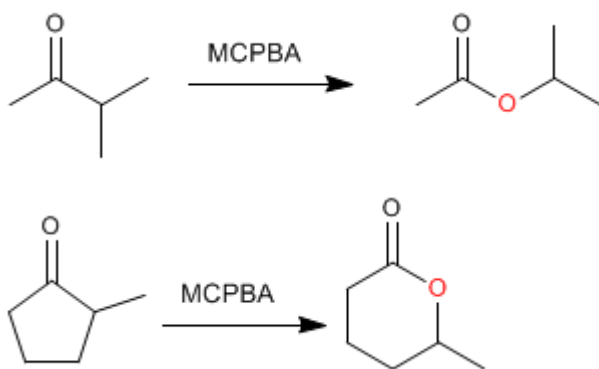


**Etapas 2.** Migración del sustituyente desde carbono carbonilo hacia el oxígeno (rojo)

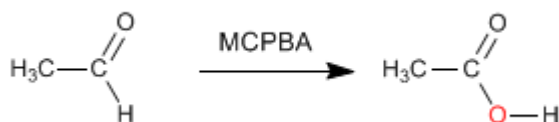


Cuando la cetona tiene dos sustituyentes diferentes migra mejor el más sustituido. Existe un orden de migración que nos ayuda a decidir que sustituyente pasa a unirse al oxígeno del perácido.

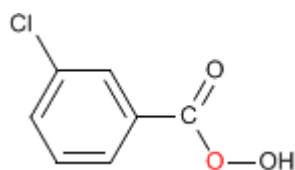
Orden de migración: H > carbono terciario > ciclohexilo > carbono secundario » fenilo > carbono primario > metilo



Como puede observarse en el orden de migración, el grupo que mejor migra, por su pequeño tamaño, es el hidrógeno, por ello, al tratar aldehídos con perácidos se produce la migración del hidrógeno formándose ácidos carboxílicos.



El **MCPBA** (Ácido meta-cloroperoxibenzoico) es un perácido ampliamente utilizado en la epoxidación de alquenos y también en Baeyer-Villger. La fórmula del MCPBA se muestra a continuación.



#### Charles Friedel (1832 - 1899)



**Origen:** Químico frances..

**Lugar de nacimiento:** Estrasburgo.

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**Docencia:** Profesor en la Universidad de la Sorbona.

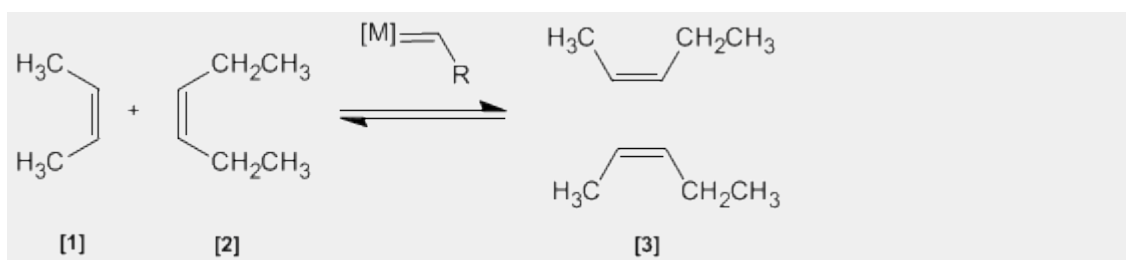
**Investigación:** Obtuvo el alcohol propílico. En 1877, Friedel y Crafts describieron por primera vez la reacción del benceno con un haloalcano en presencia de un ácido de Lewis. Esta reacción produce la alquilación del benceno y se conoce como alquilación de Friedl-Crafts.

**Premio Nobel:**

#### Metátesis de Alquenos

En esta reacción dos alquenos **[1]** y **[2]** son tratados con un metal de transición que actúa como catalizador, dando una mezcla de alquenos **[3]** (incluyendo isómeros Z/E). Este productos se obtiene por intercambio de grupos alquilideno.

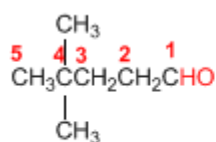




## Nomenclatura de Aldehídos y Cetonas - Reglas IUPAC

**Regla 1.** Los aldehídos se nombran reemplazando la terminación **-ano** del alcano correspondiente por **-al**. No es necesario especificar la posición del grupo aldehído, puesto que ocupa el extremo de la cadena (localizador 1).

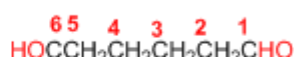
Cuando la cadena contiene dos funciones aldehído se emplea el sufijo **-dial**.



4,4-Dimetilpentanal

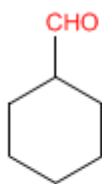


Hex-4-enal

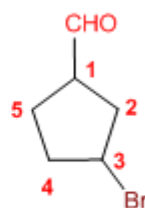


Hexanodial

**Regla 2.** El grupo **-CHO** se denomina **-carbaldehído**. Este tipo de nomenclatura es muy útil cuando el grupo aldehído va unido a un ciclo. La numeración del ciclo se realiza dando localizador 1 al carbono del ciclo que contiene el grupo aldehído.

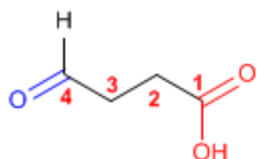


Ciclohexanocarbaldehído

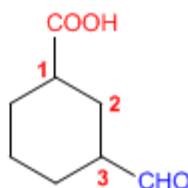


3-Bromociclopentanocarbaldehído

**Regla 3.** Cuando en la molécula existe un grupo prioritario al aldehído, este pasa a ser un sustituyente que se nombra como oxo- o formil-.



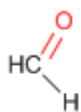
Ácido 4-oxobutanoico



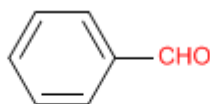
Ácido 3-formilciclohexanocarboxílico

Tanto **-carbaldehído** como **formil-** son nomenclaturas que incluyen el carbono del grupo carbonilo. **-carbaldehído** se emplea cuando el aldehído es grupo funcional, mientras que **formil-** se usa cuando actúa de sustituyente.

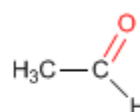
**Regla 4.** Algunos nombres comunes de aldehídos aceptados por la IUPAC son:



Formaldehído  
(Metanal)

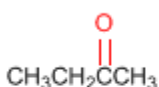


Benzaldehído  
(Benceno**carbaldehído**)

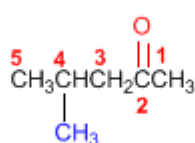


Acetaldehído  
(Etanal)

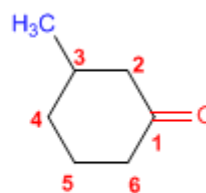
**Regla 5.** Las cetonas se nombran sustituyendo la terminación **-ano** del alcano con igual longitud de cadena por **-ona**. Se toma como cadena principal la de mayor longitud que contiene el grupo carbonilo y se numera para que éste tome el localizador más bajo.



Butan**ona**

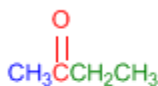


4-Metil-2-pentan**ona**

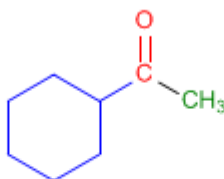


3-Metilciclohexan**ona**

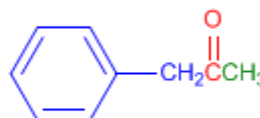
**Regla 6.** Existe un segundo tipo de nomenclatura para las cetonas, que consiste en nombrar las cadenas como sustituyentes, ordenándolas alfabéticamente y terminando el nombre con la palabra cetona.



Etil metil **cetona**

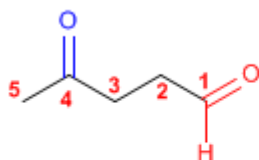


Ciclohexil metil **cetona**

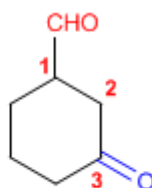


Fenil metil **cetona**

**Regla 7.** Cuando la cetona no es el grupo funcional de la molécula pasa a llamarse **OXO-**.



4-Oxopentan**al**

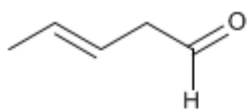


3-Oxociclohexano**carbaldehído**

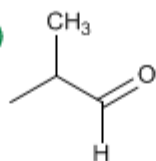
## Nomenclatura de Aldehídos y Cetonas - Problema 9.1

Nombra los siguientes aldehídos y cetonas:

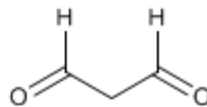
a)



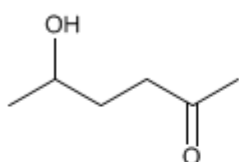
b)



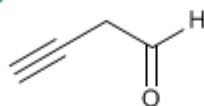
c)



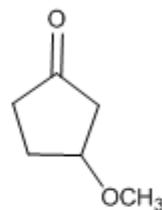
d)



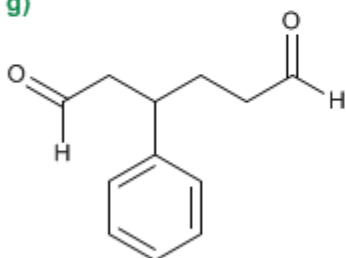
e)



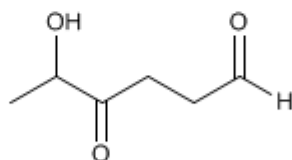
f)



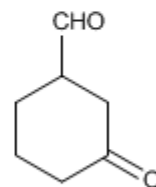
g)



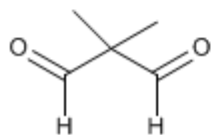
h)



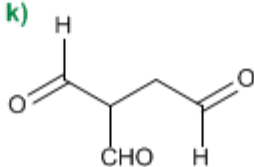
i)



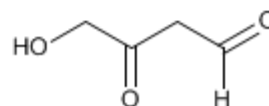
j)



k)

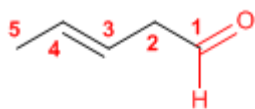


l)

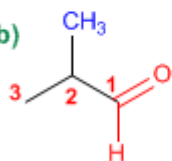


Solución

a)



b)



1. Cadena principal: 5 carbonos (pentano)

2. Numeración: comienza en el aldehído (grupo funcional)

Grupo funcional: aldehído

3. Nombre: Pent-3-enal

1. Cadena principal: 3 carbonos (propano)

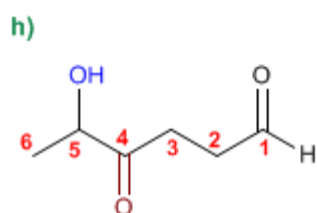
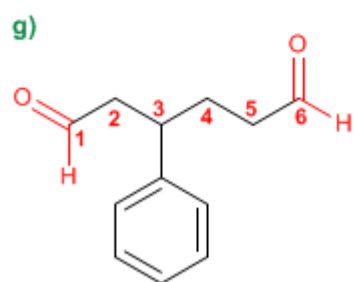
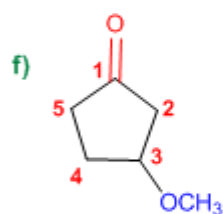
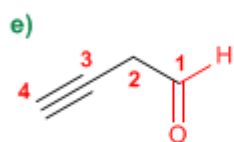
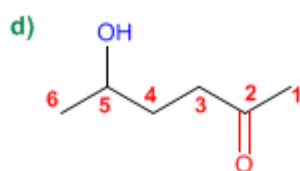
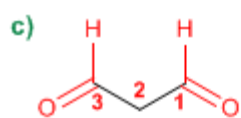
2. Numeración: localizador más bajo al aldehído.

3. Grupo funcional: aldehído

4. Sustituyentes: metilo en 2.

5. Nombre: 2-Metilpropanal

Los aldehídos y cetonas son prioritarios sobre alquenos y alquinos, y se numeran otorgándoles el localizador más bajo



1. Cadena principal: 3 carbonos (propano)
2. Grupo funcional: aldehído (dialdehído)
3. Nombre: Propanodial

1. Cadena principal: 6 carbonos (hexano)
2. Grupo funcional: cetona
3. Numeración: asignar el menor localizador a la cetona
4. Sustituyentes: hidroxí en 5.
5. Nombre: 5-Hidroxihexan-2-ona

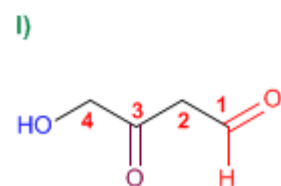
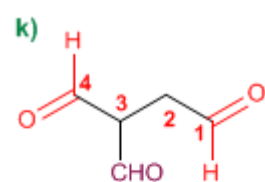
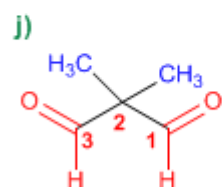
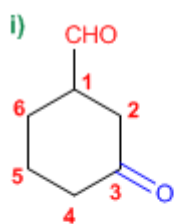
1. Cadena principal: 4 carbonos (butano)
2. Grupo funcional: aldehído
3. Numeración: asignar el menor localizador al aldehído
4. Nombre: But-3-inal

1. Cadena principal: ciclo de 5 miembros (ciclopentano)
2. Grupo funcional: cetona
3. Numeración: comienza en la cetona y prosigue hacia el sustituyente
4. Sustituyentes: metoxi en 3.
5. Nombre: 3-Metoxiciclopentanona

1. Cadena principal: 6 carbonos (hexano)
2. Grupo funcional: aldehído (dialdehído)
3. Numeración: comienza en el extremo que otorga al fenilo el localizador más bajo.
4. Sustituyentes: fenilo en 3.
5. Nombre: 3-Fenilhexanodial

1. Cadena principal: 6 carbonos (hexano)
2. Grupo funcional: aldehído
3. Numeración: asignar el menor localizador al aldehído
4. Sustituyentes: hidroxí en 5 y oxo en 4.
5. Nombre: 5-Hidroxí-4-oxohexanal

Los aldehídos son prioritarios sobre las cetonas que pasan a nombrarse como sustituyentes (oxo-)



1. Cadena principal: ciclo de 6 miembros (ciclohexano)
2. Grupo funcional: aldehído (-carbaldehído)
3. Numeración: menor localizador al grupo -CHO (este no se numera)
4. Sustituyentes: cetona (oxo-) en 3
5. Nombre: 3-Oxociclohexanocarbaldehído

1. Cadena principal: 3 carbonos (propano)
2. Grupo funcional: aldehído (dialdehído)
3. Sustituyentes: metilos en 2,2.
4. Nombre: 2,2-Dimetilpropanodial

1. Cadena principal: 4 carbonos (butano)
2. Grupo funcional: aldehído
3. Sustituyentes: formil en 3
4. Nombre: 3-Formilbutanodial

1. Cadena principal: 4 carbonos (butano)
2. Grupo funcional: aldehído
3. Numeración: asignar el menor localizador al aldehído
4. Sustituyentes: hidroxil en 4 y oxo en 3.
5. Nombre: 4-Hidroxil-3-oxobutanal



## Nomenclatura de Aldehídos y Cetonas - Problema 9.2

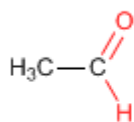
PRINT EMAIL

Dibuja la estructura de los siguientes aldehídos y cetonas:

- |   |                                  |
|---|----------------------------------|
| a) Etanal (acetaldehído)                          | g) 2,5-Dioxooctanodial           |
| b) 3-Metilbutanal                                 | h) 1,3-Ciclohexanodiona          |
| c) Benzaldehído                                   | i) 3-Metil-3-pental              |
| d) 4-Hidrox ciclohexanocarbaldehído               | j) 3-Oxobutanal                  |
| e) 3-Hidroxi-4-metil-5-oxociclohexanocarbaldehído | k) 3-Hidrox ciclopentanona       |
| f) 2-Metil-2,5-octanodiona                        | l) 4-Etoxi-5-fenil-3-oxoheptanal |

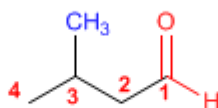
Solución

a)



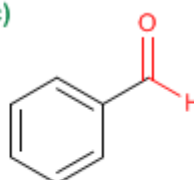
Etanal (acetaldehído)

b)

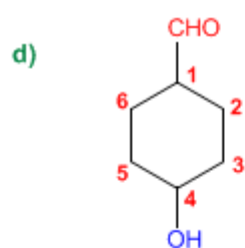


3-Metilbutanal

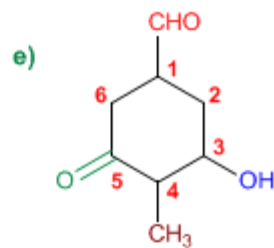
c)



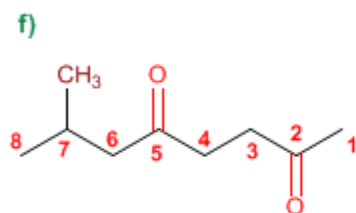
Benzaldehído



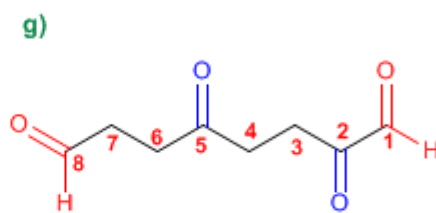
4-Hidroxiciclohexanocarbaldehído



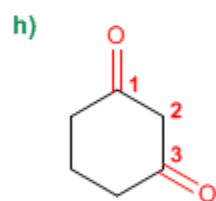
3-Hidroxi-4-metil-5-oxociclohexanocarbaldehído



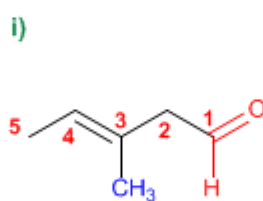
7-Metil-2,5-octanodiona



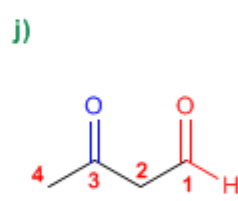
2,5-Dioxooctanal



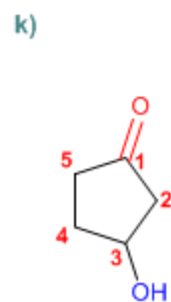
1,3-Ciclohexanodiona



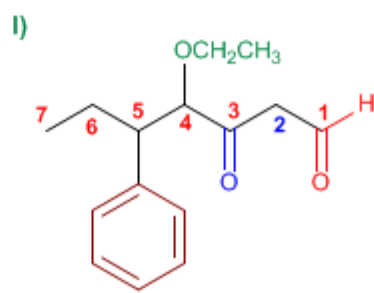
3-Metil-3-pentenal



3-Oxobutanal



3-Hidroxiciclopentanona

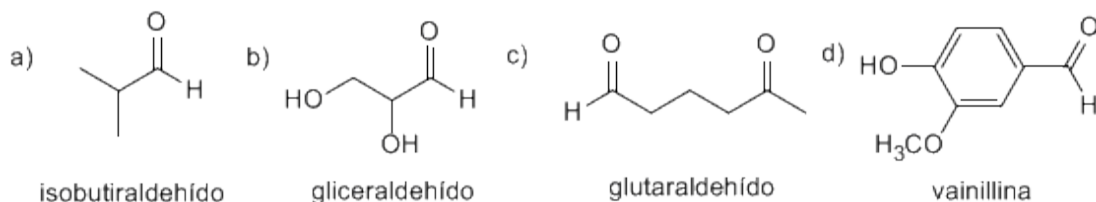


4-Etoxi-5-fenil-3-oxoheptanal

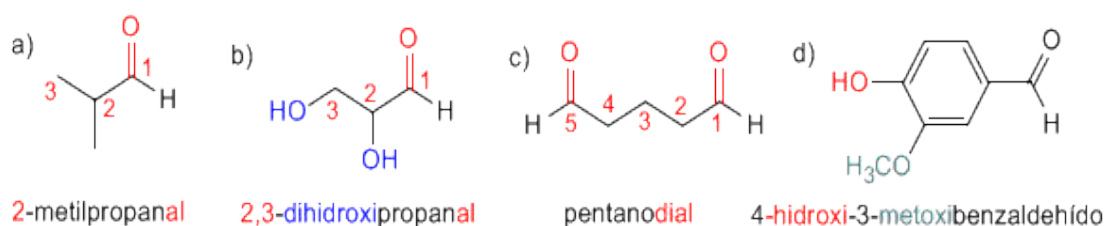
# PROBLEMAS RESUELTOS DE ALDEHÍDOS Y CETONAS

## Aldehídos y Cetonas: Problema 1

1) A continuación se dan nombres comunes y las fórmulas estructurales de algunos compuestos carbonílicos. Indique el nombre correspondiente según la IUPAC.



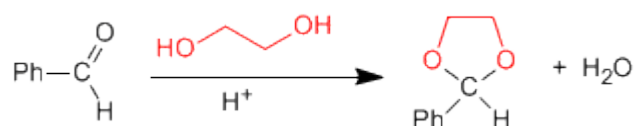
Solución



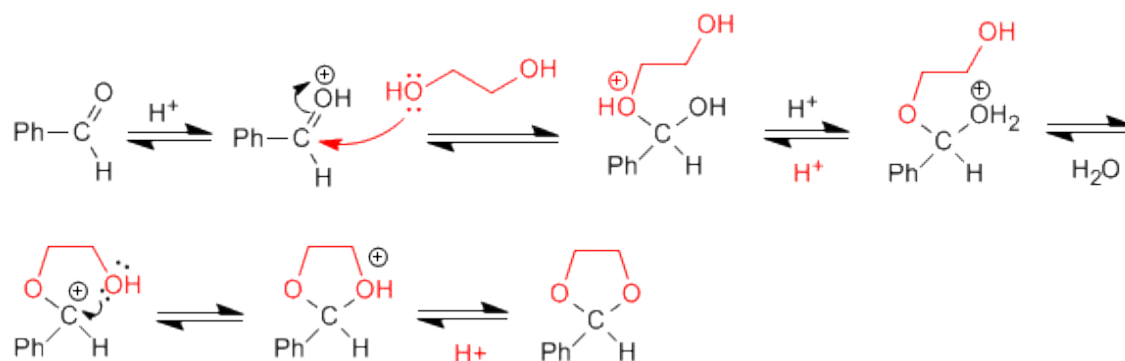
## Aldehídos y cetonas: Problema 2

Dibuje la estructura del acetal que se forma cuando el benzaldehído se calienta con 1,2-etanodiol en medio ácido. Escriba un mecanismo detallado que justifique su formación. Describa paso a paso la hidrólisis de este acetal en medio ácido acuoso.

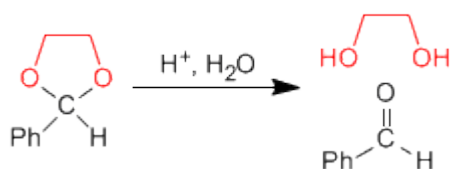
SOLUCIÓN



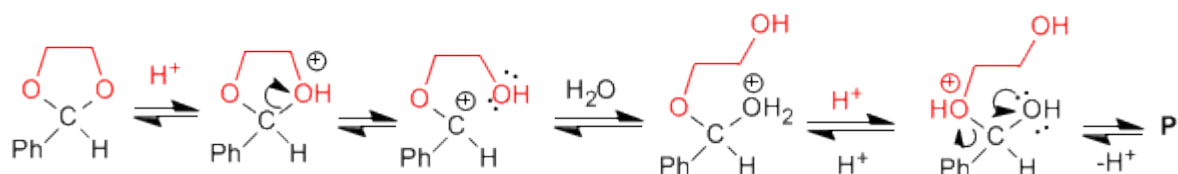
Mecanismo de formación del acetal:



La hidrólisis del acetal en medio ácido acuoso sigue es etapas inversas a la síntesis.



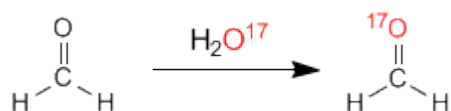
Mecanismo de hidrólisis del acetal cíclico.



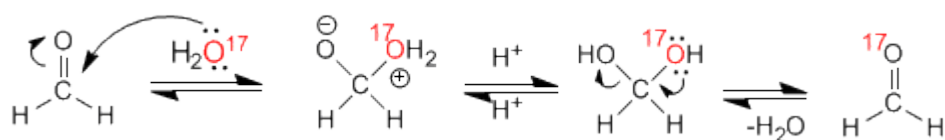
### Aldehídos y Cetonas: Problema 3

Cuando se disuelve formaldehído en agua marcada con  $^{17}\text{O}$ , se observa que después de unas horas tanto el hidrato del formaldehído como el formaldehído han incorporado el isótopo  $^{17}\text{O}$ . Sugiera una explicación razonable de este hecho.

SOLUCION



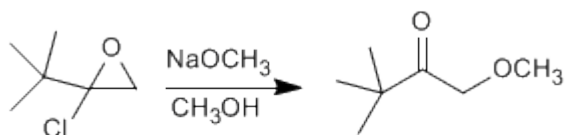
Mecanismo:



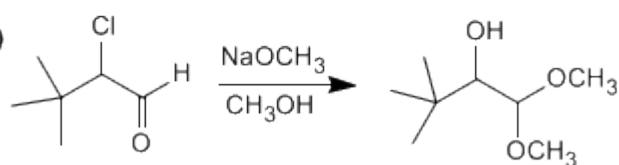
### Aldehídos y Cetonas: Problema 4

Sugiera un mecanismo razonable para una de las siguientes reacciones:

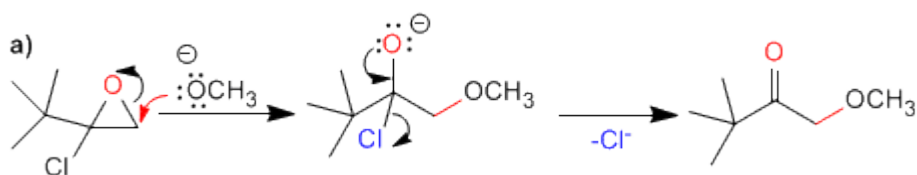
a)



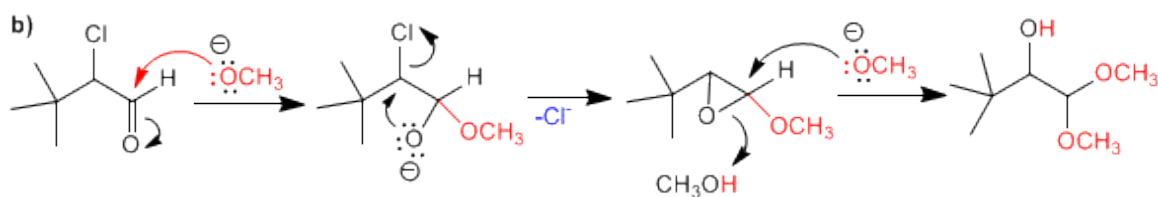
b)



## SOLUCION



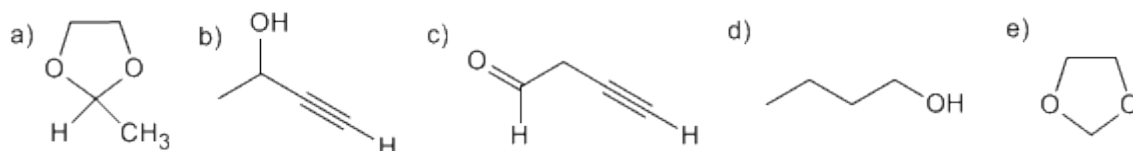
La primera etapa consiste en la apertura del oxaciclopropano sobre el carbono menos sustituido. En la segunda etapa, la cesión del par del oxígeno elimina el cloro, formándose un carbonilo.



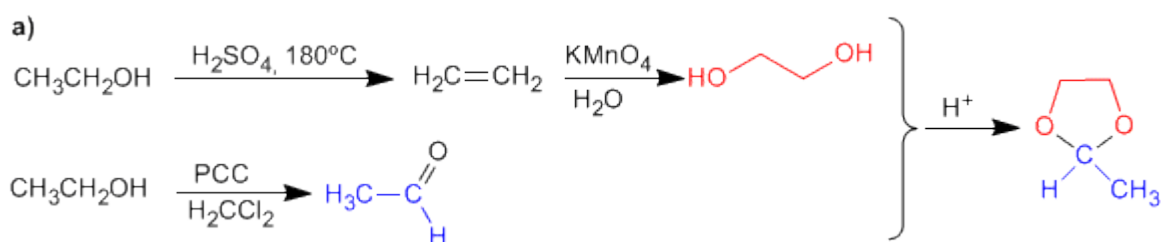
En el primer paso hay dos posibles posiciones de ataque; el carbono carbonilo y el carbono del cloro. Como el producto final no tiene metóxido en el carbono del cloro, atacamos al carbonilo. En la segunda etapa se produce una sustitución nucleófila intramolecular. Para terminar el metóxido abre el epóxido.

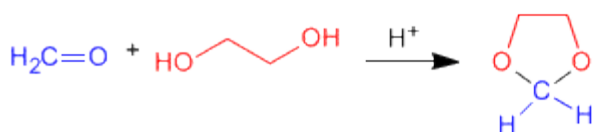
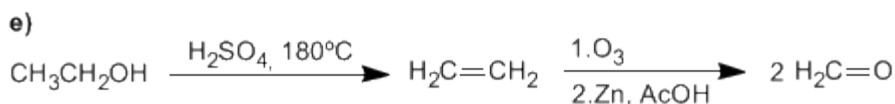
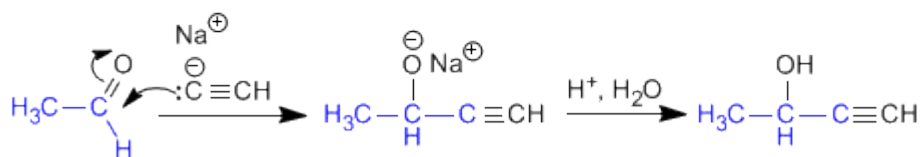
## Aldehídos y Cetonas: Problema 5

Usando etanol como fuente de todos los átomos de carbono y los reactivos que necesite, describa una síntesis eficiente de cada una de las sustancias siguientes:

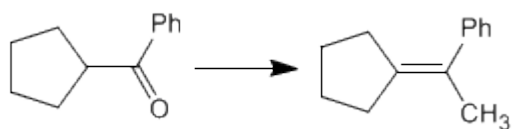


## SOLUCIÓN





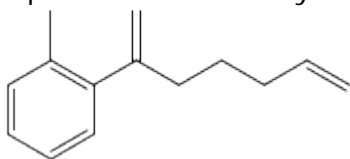
Utilizando los reactivos necesarios, indicar las etapas que permiten realizar la siguiente transformación:



[2] Isomerización en medio ácido, impulsada por la mayor estabilidad del alqueno interno.

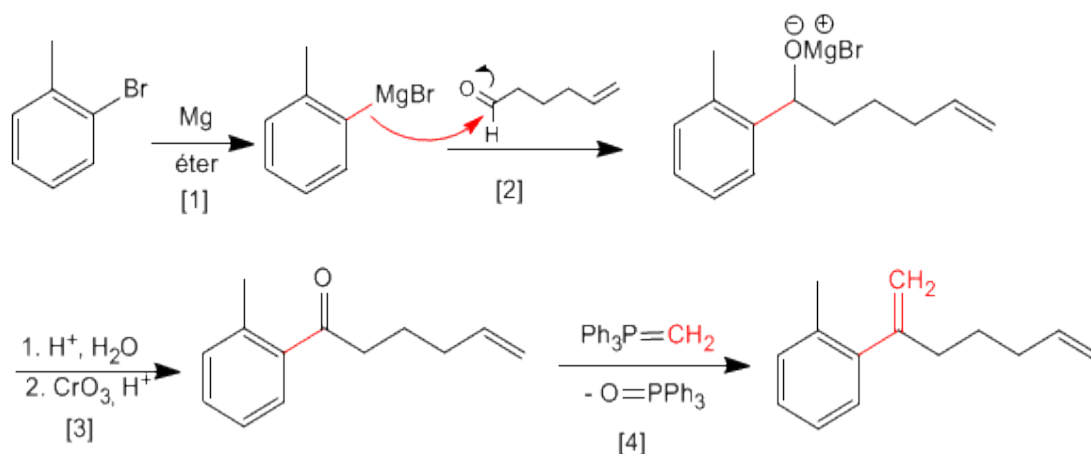
## Aldehídos y Cetonas: Problema 7

A partir de 5-hexenal y o-bromotolueno obtener el siguiente producto.



Pueden ser necesarios reactivos orgánicos e inorgánicos adicionales.

SOLUCIÓN



[1] Formación del magnesiano

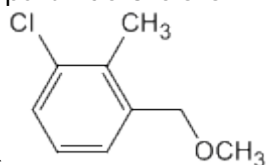
[2] Ataque nucleófilo del magnesiano al carbonilo.

[3] Hidrólisis y posterior oxidación del alcohol secundario.

[4] Reacción de Wittig entre la cetona y el trifenilmetilenfosforano.

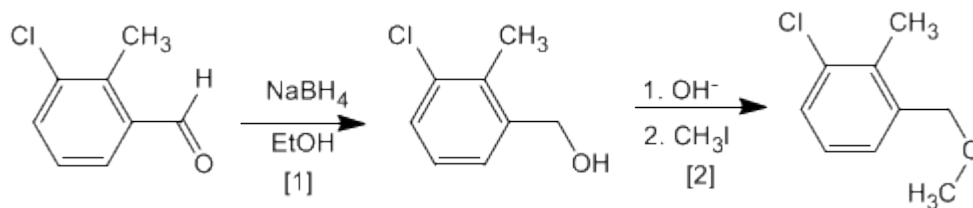
## Aldehídos y Cetonas: Problema 8

Obtener a partir de 3-cloro-2-metilbenzaldehído y de los reactivos



necesarios  
el compuesto siguiente:

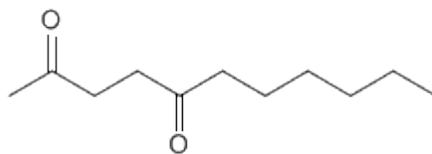
SOLUCIÓN



[1] Reducción del aldehído a alcohol

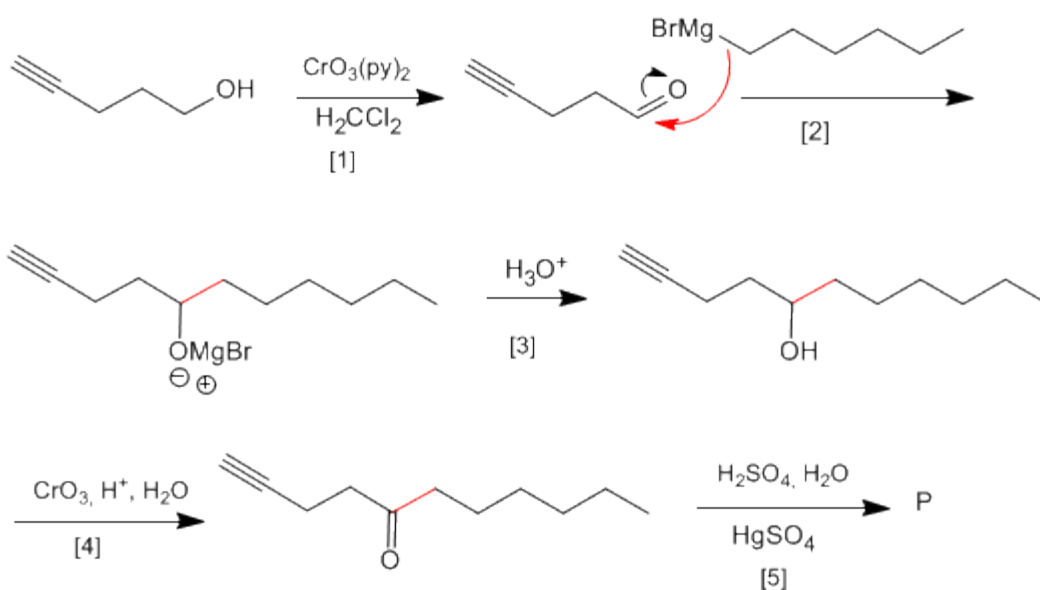
[2] Síntesis de Williamson de éteres.

## Aldehídos y Cetonas: Problema 9



A partir de 4-pentin-1-ol obtener:

SOLUCIÓN



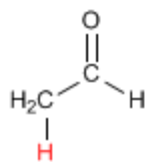
- [1] Oxidación del alcohol a aldehído
- [2] Formación del enlace carbono-carbono mediante organometálicos de magnesio
- [3] Protonación del alcohol
- [4] Oxidación del alcohol con Jones (Puedes utilizar también  $\text{CrO}_3(\text{py})_2$ )
- [5] Hidratación Markovnikov del alquino, para formar cetonas



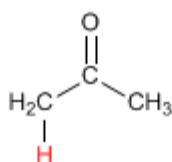
# TEORÍA DE ENOLES Y ENOLATOS

## Formación de Enolatos

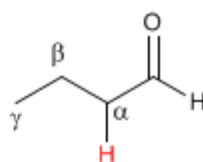
Los aldehídos y cetonas presentan hidrógenos ácidos en la posición vecina al grupo carbonilo, conocida como posición alfa. Estos hidrógenos presentan un pKa comprendido entre 18 y 21.



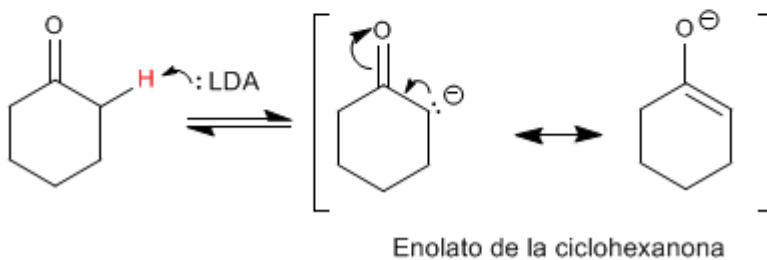
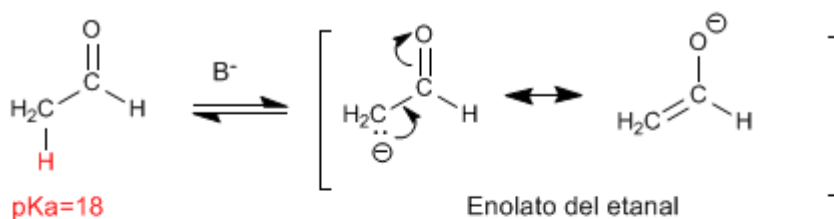
pKa=18



pKa=20-21



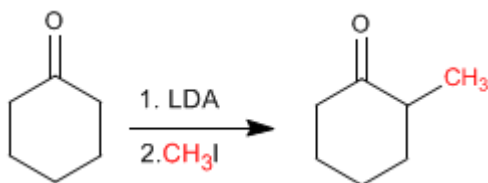
La acidez de los hidrógenos  $\alpha$  es debida a la estabilización de la base conjugada (enolato) por resonancia.



## Alquilación de Enolatos

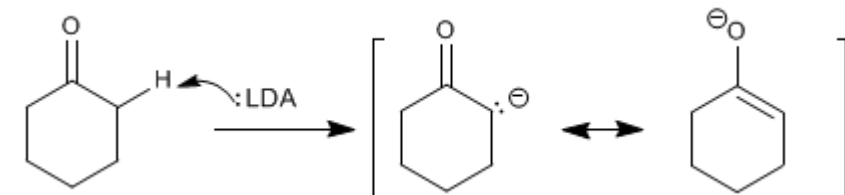
Los enolatos actúan como nucleófilos a través del carbono atacando a un gran número de electrófilos (haloalcanos, epóxidos, carbonilos, ésteres.....). En este punto nos fijaremos en la reacción entre enolatos y haloalcanos, que permite añadir cadenas carbonadas a la posición  $\alpha$  de la cadena.

La Ciclohexanona se convierte en 2-Metilciclohexanona por tratamiento con LDA seguido de yoduro de metilo.

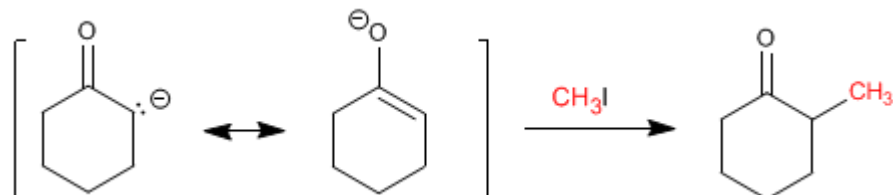


Etapas del mecanismo por el que se alquila la ciclohexanona:

### Etapas del mecanismo

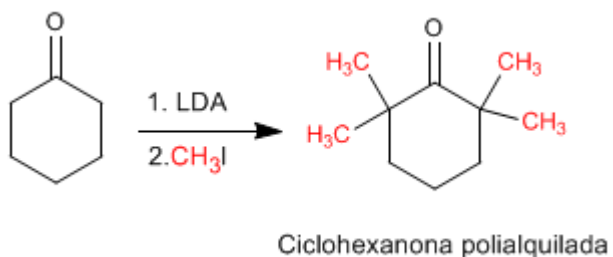


### Etapas del mecanismo



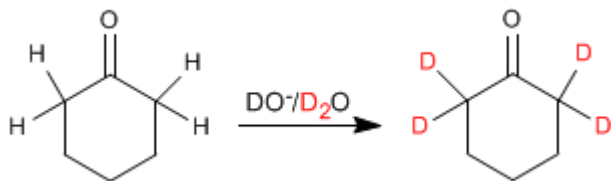
Las reacciones de alquilación tienen dos importantes problemas.

1. Competencia con la condensación aldólica. Los carbonilos en medio básico tienden a condensar para formar aldoles.
2. La reacción es difícil de controlar y tiende a polialquilar el carbonilo.



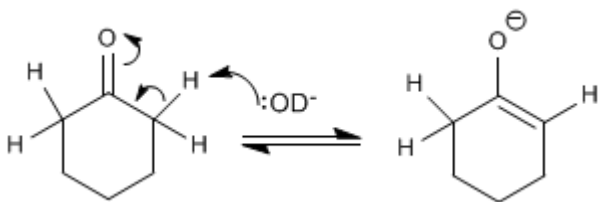
## Intercambio hidrógeno - Deuterio

Los aldehídos y cetonas intercambian sus hidrógenos a por deuterios cuando se tratan con  $\text{DO}^-/\text{D}_2\text{O}$  o con  $\text{D}^+/\text{D}_2\text{O}$ . En medios básicos la reacción transcurre a través de enolatos y en medios ácidos los intermediarios formados son enoles.

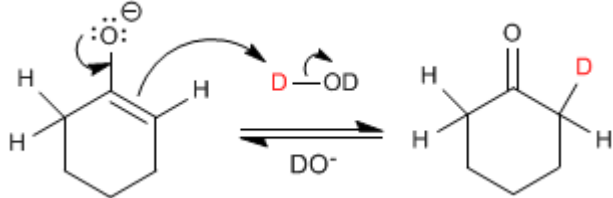


El mecanismo del intercambio hidrógeno-deuterio transcurre en los siguientes pasos:

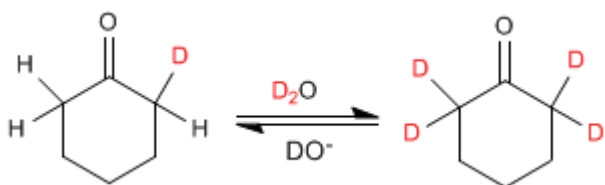
**Etapas 1.** Formación del enolato



**Etapas 2.** Transferencia del deuterio al enolato



**Etapas 3.** Sustitución del resto de hidrógenos



## Halogenación de aldehídos y cetonas

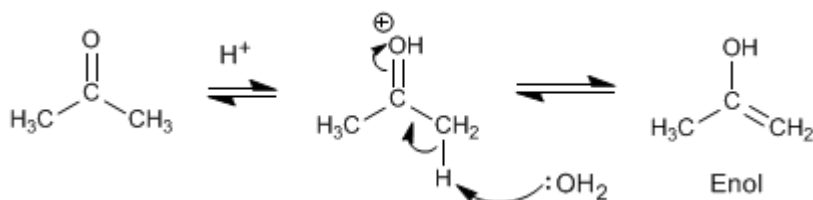
Los aldehídos y cetonas reaccionan con halógenos en medios ácidos o básicos produciéndose la sustitución de hidrógenos a por halógenos.

Halogenación de la propanona en medio ácido:

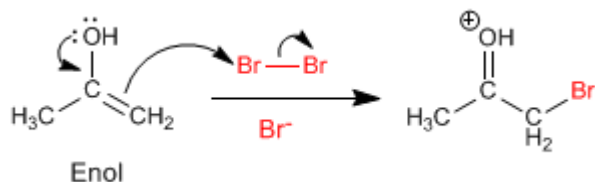


El mecanismo de halogenación en **medio ácido** tiene las siguientes etapas:

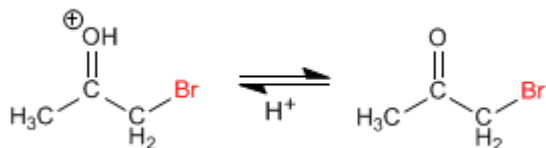
**Etapas 1.** Formación del enol



**Etapas 2.** Ataque nucleófilo del enol sobre el halógeno ayudado por la cesión del para del oxígeno.

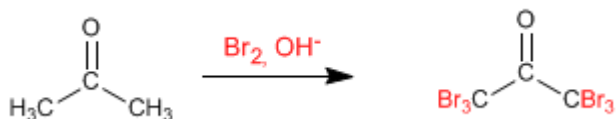


**Etapas 3.** Desprotonación



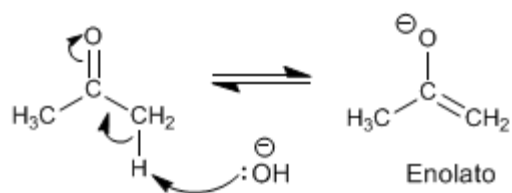
Trabajando con un equivalente de reactivo la halogenación para en una primera adición y no ocurren polihalogenaciones. El paso clave del mecanismo es la formación del enol y esta etapa requiere protonar el oxígeno del carbonilo. Una vez halogenada la posición  $\alpha$  el oxígeno se vuelve menos básico, debido al efecto electronegativo del bromo, protonándose peor.

Halogenación de la propanona en **medio básico**:

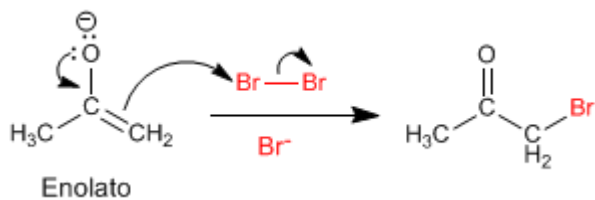


La halogenación en medio básico tiene el siguiente mecanismo:

**Etapla 1.** Formación del enolato



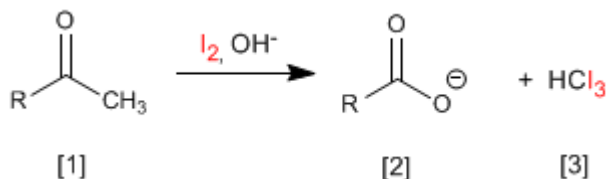
**Etapla 2.** Ataque nucleófilo del enolato sobre el halógeno ayudado por la cesión del para del oxígeno.



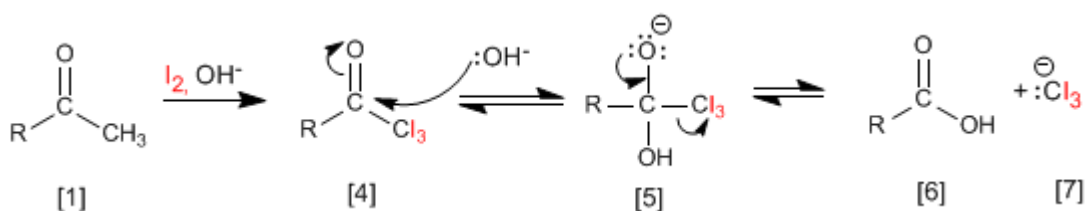
Este mecanismo se repite otras 5 veces sustituyendo todos los hidrógenos a por halógenos. En este caso la reacción no para puesto que el producto halogenado es más reactivo que la propanona de partida. La base arranca mejor los hidrógenos en el producto halogenado (son más ácidos), haciendo imposible parar la reacción.

## Reacción del Haloformo (Yodoformo)

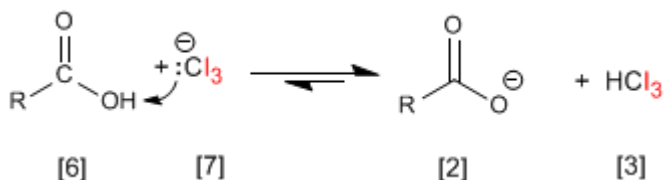
Las cetonas metílicas **[1]** reaccionan con halógenos en medios básicos generando carboxilatos **[2]** y haloformo **[3]**.



El mecanismo consiste en halogenar completamente el metilo, sustituyendo en una etapa posterior el grupo  $-\text{CX}_3$  formado por  $-\text{OH}$ .



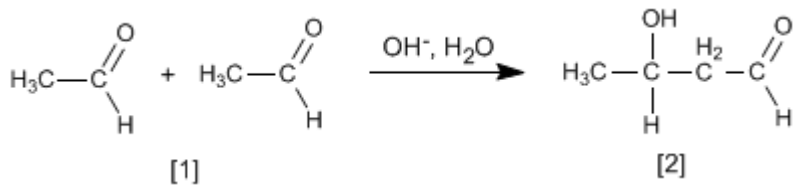
El grupo  $\text{Cl}_3^\ominus$  es muy básico y desprotona el ácido carboxílico formándose yodoformo y el carboxilato.



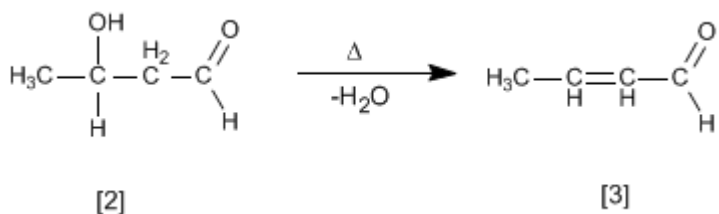
Esta reacción (con yodo) puede emplearse como ensayo analítico para identificar cetonas metílicas aprovechando que el yodoformo precipita de color amarillo.

## Condensación Aldólica

Aldehídos y cetonas [1] condensan en medios básicos formando aldoles [2]. Esta reacción se denomina condensación aldólica.

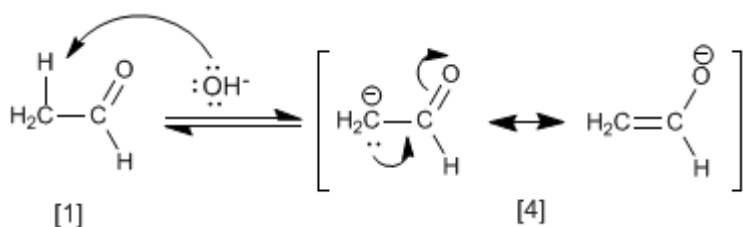


El aldol [2] formado deshidrata en el medio básico por calentamiento para formar un  $\alpha,\beta$ -insaturado [3].



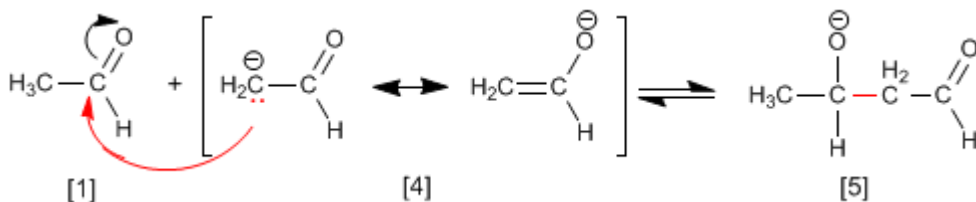
El mecanismo de la condensación aldólica transcurre con formación de un enolato, que ataca al carbonilo de otra molécula. En esta condensación se forma un enlace carbono-carbono entre el carbonilo de una molécula y el carbono  $\alpha$  de la otra.

### Etapa 1. Formación del enolato

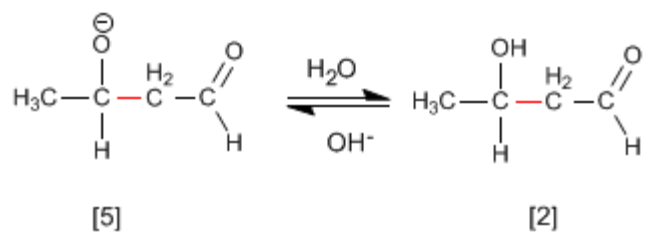


La base desprotona el carbono alfa del etanal [1] generando el enolato [4] estabilizado por resonancia.

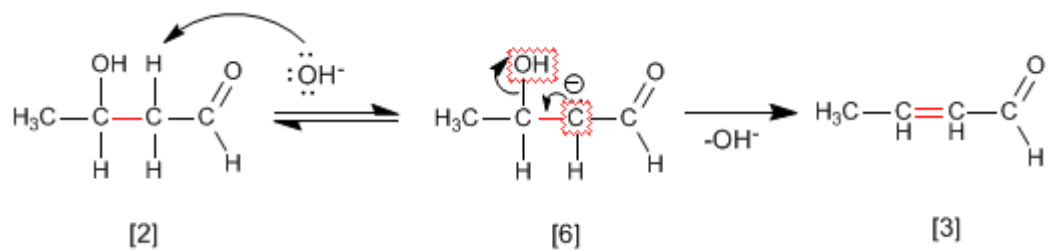
### Etapa 2. Ataque nucleófilo del enolato sobre el carbonilo



**Etapas 3.** Protonación



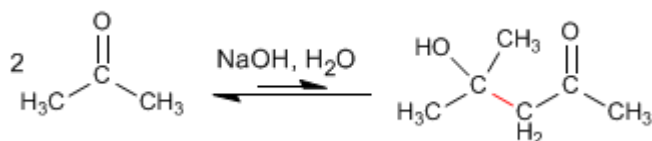
**Etapas 4.** Deshidratación del aldol



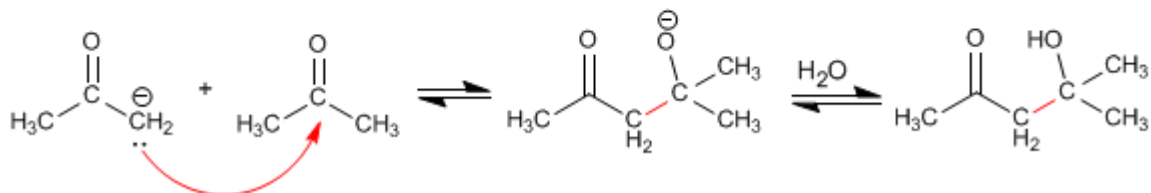
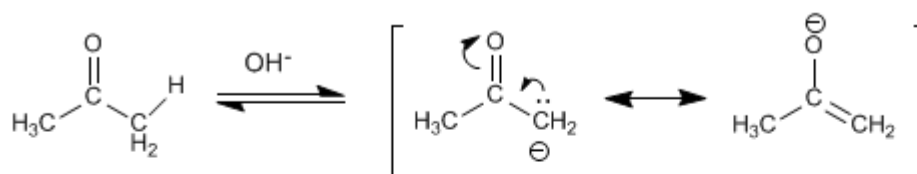


## Condensación aldólica con cetonas

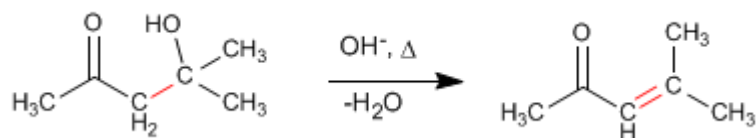
Las cetonas son menos reactivas que los aldehídos y dan un rendimiento muy bajo en la condensación aldólica. Así, dos moléculas de propanona condensan para formar el aldol correspondiente con un rendimiento del 2%. Se pueden conseguir porcentajes elevados del producto separándolo del medio de reacción según se va formando, o bien, calentando para deshidratarlo. De ambas formas los equilibrios de la aldólica se desplazan hacia el producto final.



**Mecanismo de la reacción:**



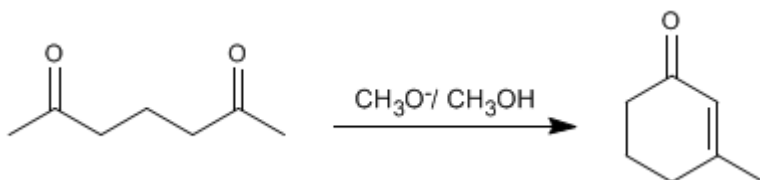
La deshidratación final permite el desplazamiento de los equilibrios. También se puede realizar una extracción del aldol del medio de reacción para favorecer la reacción.



## Condensación aldólica intramolecular

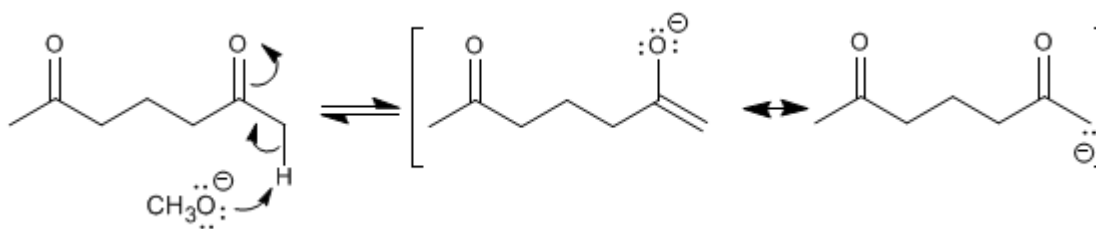
Los compuestos dicarbonílicos condensan mediante la aldólica intramolecular en medios básicos. En esta reacción se obtienen ciclos de cinco o seis miembros.

Así, la 2,6-heptanodiona condensa con metóxido en metanol para formar el 3-metilciclohex-2-enona.

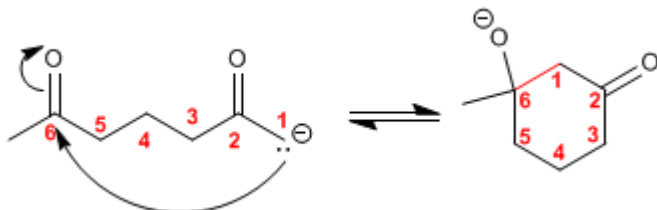


El mecanismo de la reacción transcurre a través de las siguientes etapas:

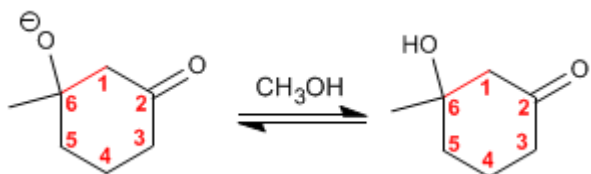
**Etapas 1.** Formación del enolato.



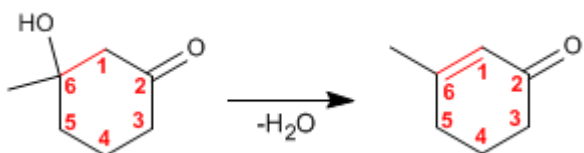
**Etapas 2.** Adición nucleófila intramolecular



**Etapas 3.** Protonación de la base del aldol



**Etapas 4.** Deshidratación del aldol

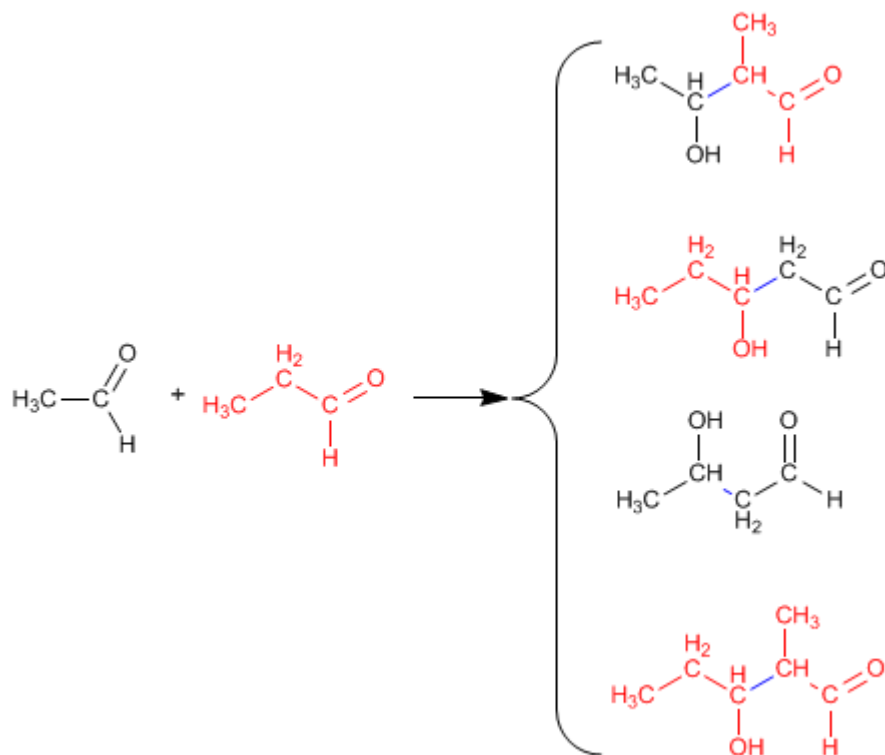


## Condensación aldólica cruzada o mixta

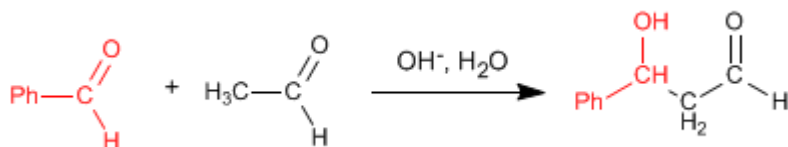
La reacción entre dos carbonilos diferentes se llama aldólica cruzada o mixta. Esta reacción sólo tiene utilidad sintética en dos casos:

1. Sólo uno de los carbonilos puede formar enolatos.
2. Uno de los carbonilos es mucho más reactivo que el otro.

En el resto de situaciones la aldólica mixta genera mezclas de cuatro productos. Veamos como ejemplo la condensación del etanal y propanal.

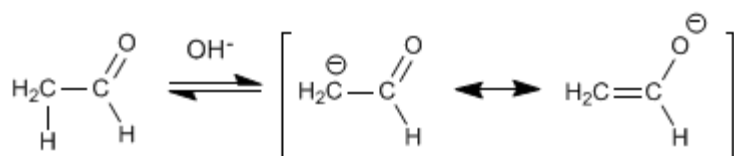


La condensación aldólica mixta del etanal con el benzaldehído genera un producto, cuando se trabaja en exceso de benzaldehído, debido a que el benzaldehído carece de hidrógenos en el carbono alfa y no puede formar enolatos.



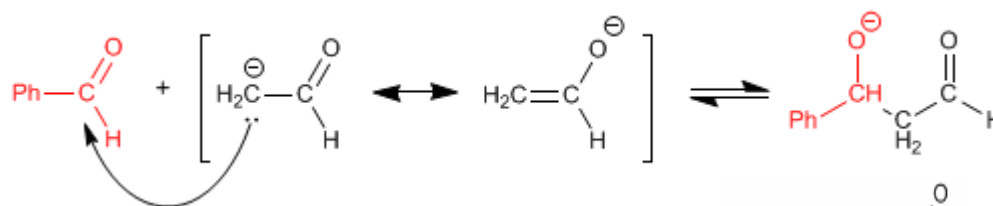
El mecanismo de esta reacción tiene lugar en las siguientes etapas:

### Etapla 1. Enolización del etanal

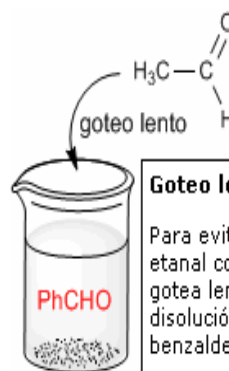
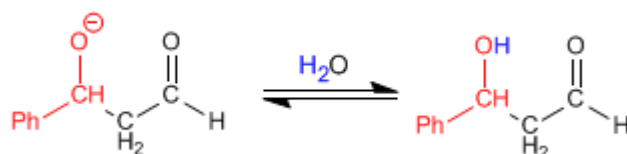


La formación de enolatos sólo puede tener lugar con el etanal, puesto que el benzaldehído carece de hidrógenos ácidos en el carbono alfa.

### Etapla 2. Ataque nucleófilo del enolato al benzaldehído.



En esta etapa puede ocurrir el ataque del enolato de etanal sobre si mismo. Para evitarlo debe trabajarse en exceso de benzaldehído. Un procedimiento experimental muy usado para evitar la condensación del etanal consigo mismo es gotear lentamente el etanal sobre una disolución básica de benzaldehído

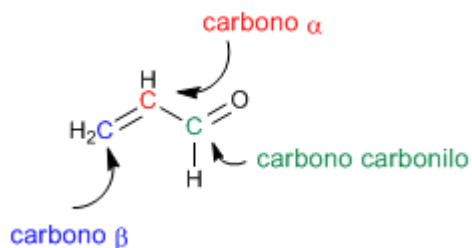


#### Goteo lento

Para evitar la condensación del etanal consigo mismo, se gotea lentamente sobre una disolución básica de benzaldehído.

## Síntesis de carbonilos alfa,beta-insaturados

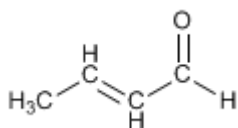
Los carbonilos  $\alpha,\beta$ -insaturados son compuestos orgánicos que tienen un doble enlace entre las posiciones  $\alpha,\beta$  de un aldehído o cetona.



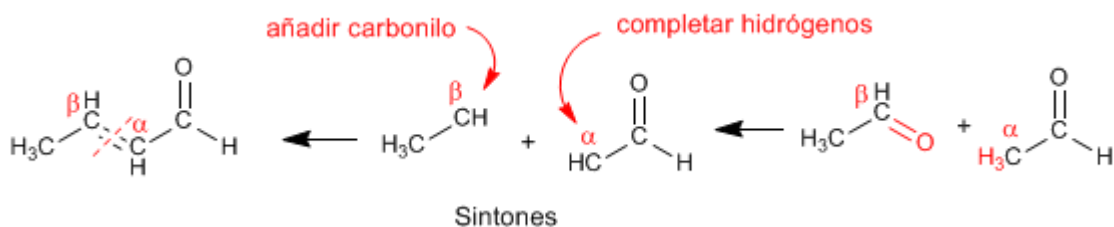
El propenal o acroleína es un carbonilo  $\alpha,\beta$ -insaturado. Sus dos dobles enlaces conjugados le confieren una reactividad especial.

Existen 4 métodos importantes para la preparación de  $\alpha,\beta$ -insaturados: condensación aldólica, halogenación del carbono  $\alpha$  seguida de eliminación, oxidación de alcoholes alílicos y Wittig.

**Método 1.** Preparar mediante la condensación aldólica el siguiente compuesto.

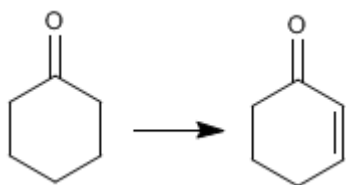


Empleamos la retrosíntesis para preparar el compuesto. Al ser de la familia de los  $\alpha,\beta$ -insaturados se puede obtener mediante la condensación aldólica.

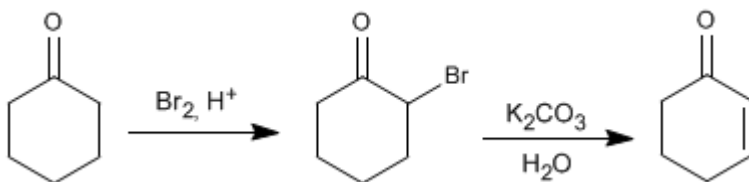


Para obtener los reactivos que forman el  $\alpha,\beta$ -insaturado se rompe por el doble enlace, obteniéndose los sintones (equivalentes sintéticos). Los reactivos se obtienen añadiendo al carbono  $\beta$  un carbonilo y completando los hidrógeno que faltan en el carbono  $\alpha$ .

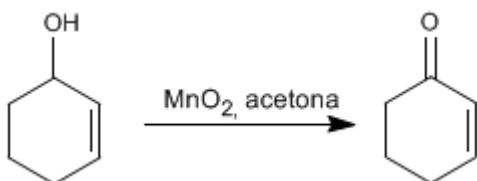
**Ejemplo 2.** Indicar como se puede realizar las siguiente transformación.



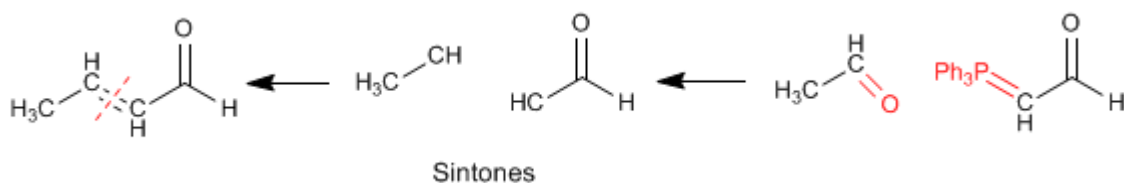
En una primera etapa se halogena la posición  $\alpha$  del carbonilo. En la segunda etapa se realiza una eliminación que nos deja el producto final.



**Método 3.** La oxidación de alcoholes alílicos con dióxido de manganeso en acetona produce  $\alpha,\beta$ -insaturados



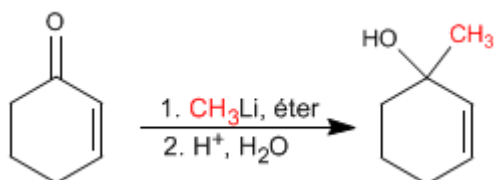
**Método 4.** Reacción de Wittig



## Reactividad de carbonilos alfa,beta-insaturados

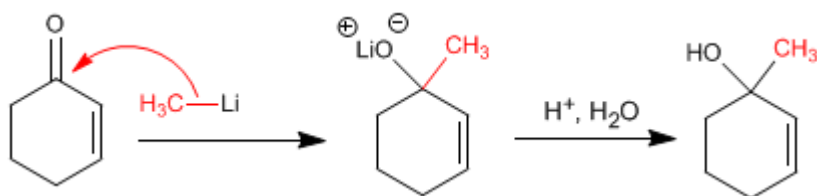
Los  $\alpha,\beta$ -insaturados son compuestos que poseen dos posiciones electrófilas: el carbono carbonilo y el carbono  $\beta$ .

**Adiciones 1,2.** Los organometálicos de litio atacan al carbono carbonilo dando lugar a adiciones 1,2.



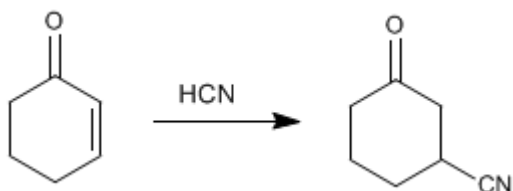
Los organometálicos de litio y magnesio atacan al carbono carbonilo de los  $\alpha,\beta$ -insaturados

Mecanismo de la adición 1,2

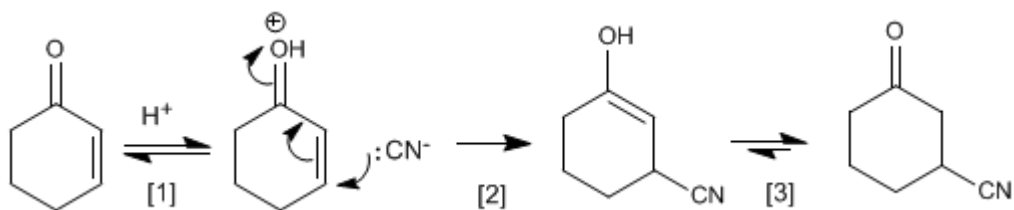


**Adiciones 1,4.** Los cupratos, cianuro y otros nucleófilos atacan al carbono  $\beta$  de los  $\alpha,\beta$ -insaturados, dando adiciones 1,4.

El ácido cianhídrico da adiciones 1,4 con los  $\alpha,\beta$ -insaturados. El ciano se une al carbono  $\beta$ .

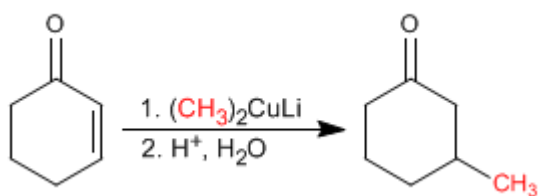


Mecanismo de adición del ácido cianhídrico a la Ciclohex-2-enona

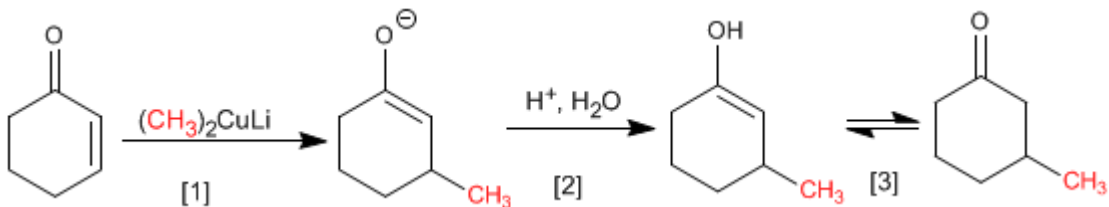


- [1] Protonación del carbonilo
- [2] Ataque nucleófilo del cianuro al carbono  $\beta$ .
- [3] Tautomería ceto-enol.

Los cupratos son organometálicos de cobre que se adicionan al carbono  $\beta$  de los  $\alpha,\beta$ -insaturados.



El mecanismo de la reacción comienza con el ataque nucleófilo del cuprato sobre el carbono  $\beta$ , formando un enolato, que se protona en la segunda etapa para dar un enol. El enol tautomeriza a cetona generando el producto final.

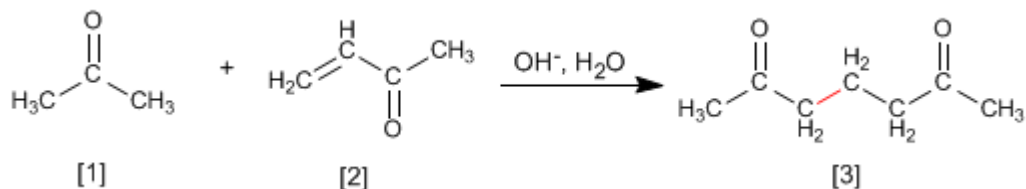


- [1] Adición nucleófila del cuprato.
- [2] Protonación del enolato
- [3] Tautomería ceto-enol



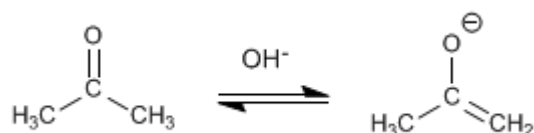
## Adición de Michael y anelación de Robinson

Los enolatos de aldehídos o cetonas se adicionan a los  $\alpha,\beta$ -insaturados para formar 1,5-dicarbonilos. Esta reacción se denomina adición de Michael.

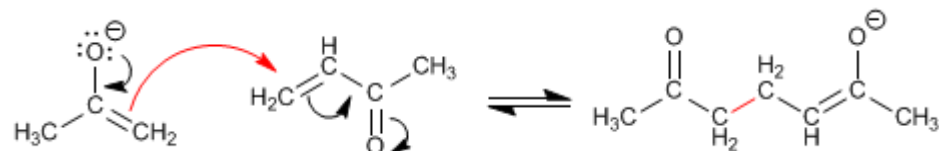


La propanona [1] reacciona con el  $\alpha,\beta$ -insaturado [2] para formar el 1,5-dicarbonilo [3]  
Mecanismo de la Adición de Michael:

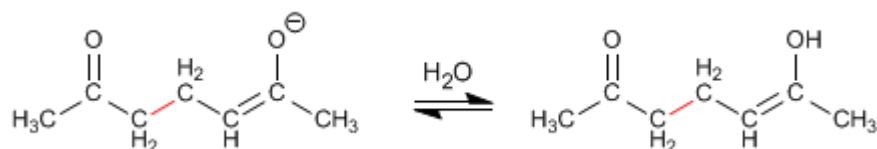
**Etapas 1.** Formación del enolato.



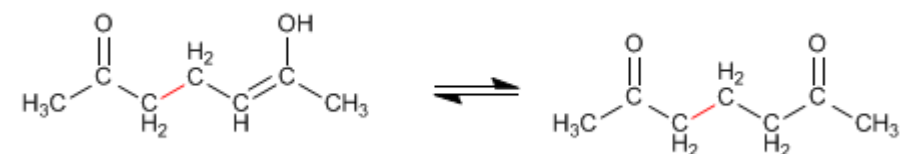
**Etapas 2.** Ataque nucleófilo del enolato al carbono  $\beta$  del  $\alpha,\beta$ -insaturado.



**Etapas 3.** Equilibrio ácido-base



**Etapas 4.** Tautomería ceto-enol

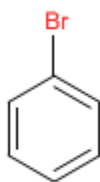


El producto de Michael puede condensar mediante una aldólica intramolecular, formando un  $\alpha,\beta$ -insaturado. El conjunto de la adición de Michael y la aldólica final se conoce como reacción de Robinson

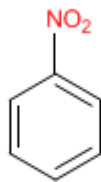
# TEORÍA DEL BENCENO

## Nomenclatura del Benceno

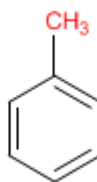
Los bencenos monosustituídos se nombran terminando el nombre del sustituyente en benceno.



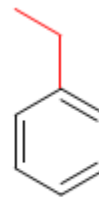
Bromobenceno



Nitrobenceno

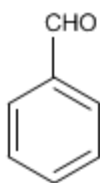


Metilbenceno

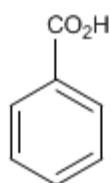


Etilbenceno

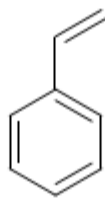
Algunos derivados monosustituídos del benceno tienen nombres comunes ampliamente aceptados.



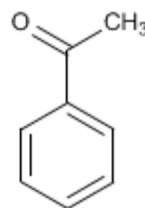
Benzaldehído



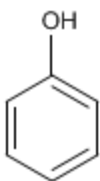
Ácido benzoico



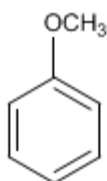
Estireno



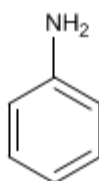
Acetofenona



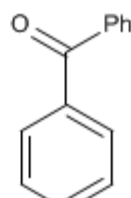
Fenol



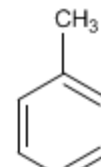
Anisol



Anilina

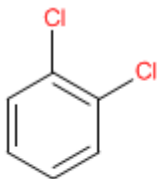


Benzofenona

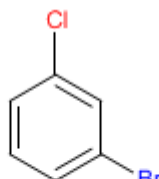


Tolueno

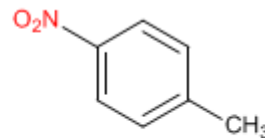
En bencenos disustituídos se emplean los prefijos *orto* (benceno 1,2-disustituído), *meta* (benceno 1,3-disustituído) y *para* (benceno 1,4-disustituído) para indicar la posición de los sustituyentes en el anillo.



o-Diclorobenceno  
(1,2-Diclorobenceno)



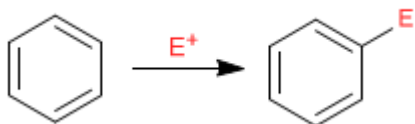
m-Bromoclorobenceno  
(1-Bromo-3-clorobenceno)



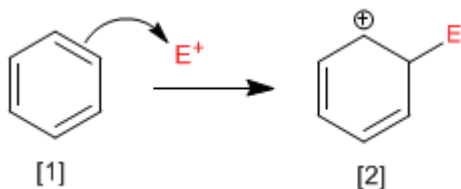
p-Nitrotolueno  
(4-Nitrotolueno)

## Sustitución Electrónica Aromática

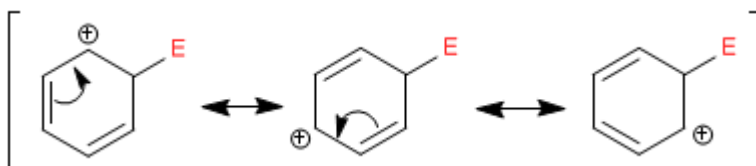
El benceno actúa como nucleófilo, atacando a un número importante y variado de electrófilos.



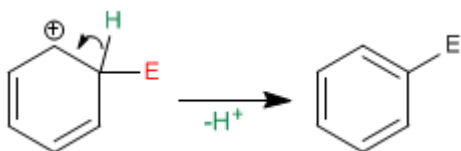
**Etapas 1.** En la primera etapa de la reacción el electrófilo acepta un par de electrones procedentes de la nube  $\pi$  del benceno, formándose un carbocatión estabilizado por resonancia.



El catión ciclohexadienilo [2] deslocaliza la carga positiva según las siguientes estructuras:

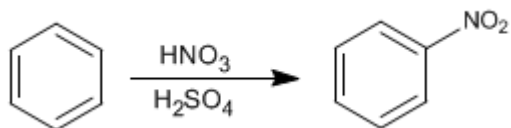


**Etapas 2.** En la segunda etapa el benceno recupera su aromaticidad por pérdida de un protón. Es una etapa rápida conocida como rearomatización del anillo.

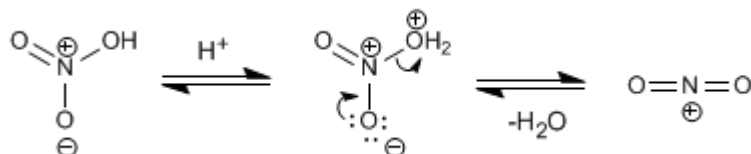


## Nitración del Benceno

El benceno reacciona con la mezcla nítrico-sulfúrica adicionando grupos nitro.

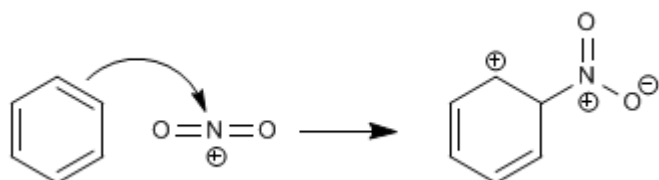


El electrófilo de esta reacción es el catión nitronio,  $\text{NO}_2^+$ . Las concentraciones de este catión en el ácido nítrico son muy bajas para nitrar el benceno, por ello es necesario añadir ácido sulfúrico.

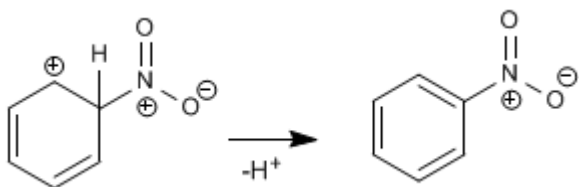


**Mecanismo para la nitración del benceno:**

**Etapla 1.** Ataque del benceno al catión nitronio

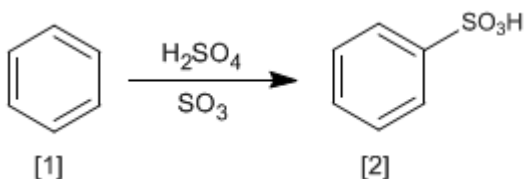


**Etapla 2.** Recuperación de la aromaticidad por pérdida de un protón



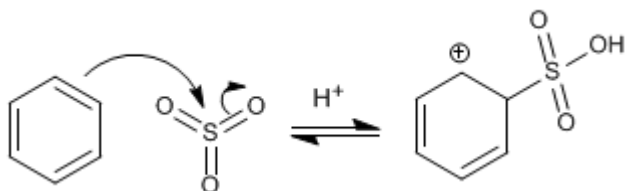
## Sulfonación del Benceno

La reacción del benceno [1] con una disolución de trióxido de azufre en ácido sulfúrico produce ácidos bencenosulfónicos [2].

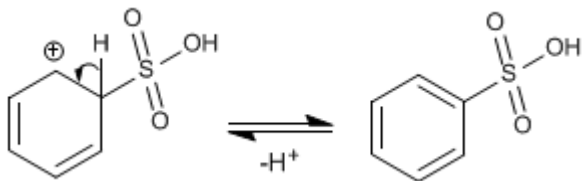


El mecanismo de la sulfonación tiene lugar con las siguientes etapas:

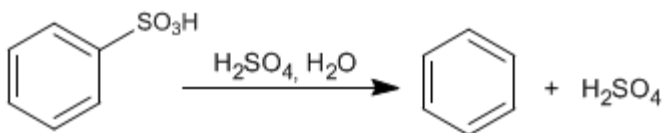
**Etapas 1.** Ataque del benceno al trióxido de azufre



**Etapas 2.** Recuperación de la aromaticidad por pérdida de un protón.

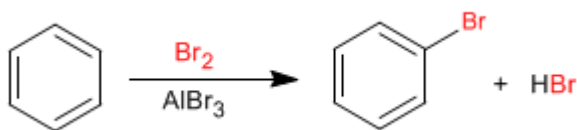


El mecanismo de la sulfonación es reversible, lo cual permite eliminar el grupo  $-\text{SO}_3\text{H}$  por tratamiento con sulfúrico acuoso. Esta propiedad es utilizada para proteger posiciones del benceno, ocupándolas con el grupo  $-\text{SO}_3\text{H}$ .



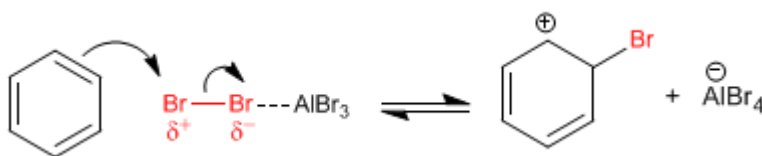
## Halogenación del Benceno

El benceno reacciona con halógenos en presencia de ácidos de Lewis para formar derivados halogenados.

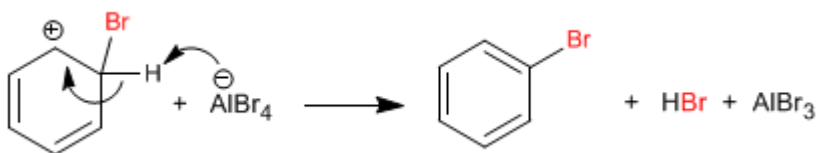


El mecanismo de la halogenación tiene lugar con las siguientes etapas:

**Etapas 1.** La molécula de bromo se polariza al interactuar con el ácido de Lewis. El benceno ataca al bromo polarizado positivamente para formar el catión ciclohexadienilo.



**Etapas 2.** Recuperación de la aromaticidad por pérdida de un protón.

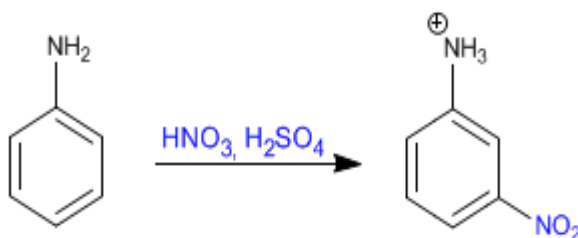


La cloración se puede llevar a cabo de forma similar a la bromación. La reacción con flúor y yodo se realiza muy poco frecuentemente. En el caso del flúor la reacción es difícil de controlar por su elevada reactividad. Por el contrario, el yodo reacciona lentamente y tiene un equilibrio desfavorable.

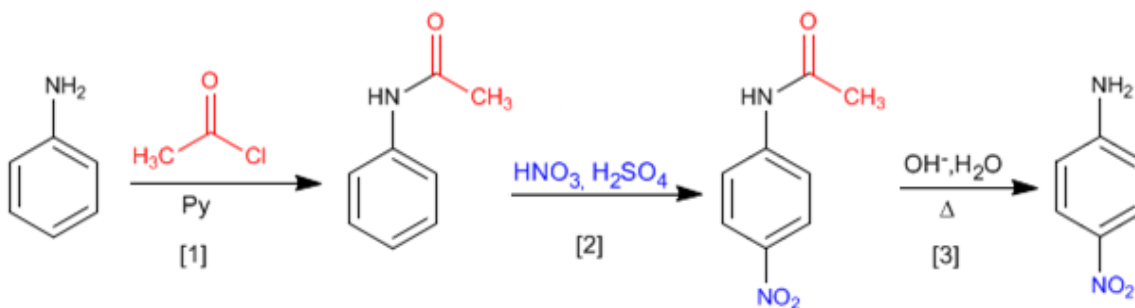
## Benceno - Protección y desprotección del grupo amino

El grupo amino es un activante fuerte, que orienta a orto/para. Sin embargo, en medios ácidos se protona transformándose en un desactivante fuerte (sal de amonio) que orienta a posición meta. Se puede evitar la protonación del amino protegiéndolo con cloruro de etanoilo en piridina.

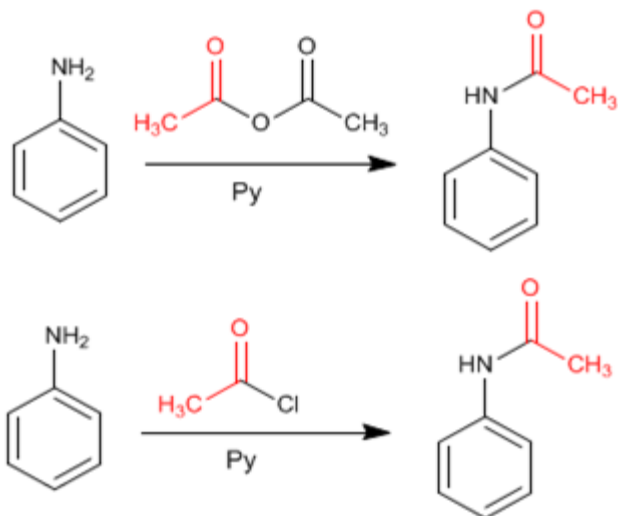
Nitración de la anilina sin protección del amino



Nitración de la anilina con protección del grupo amino, empleando cloruro de etanoilo

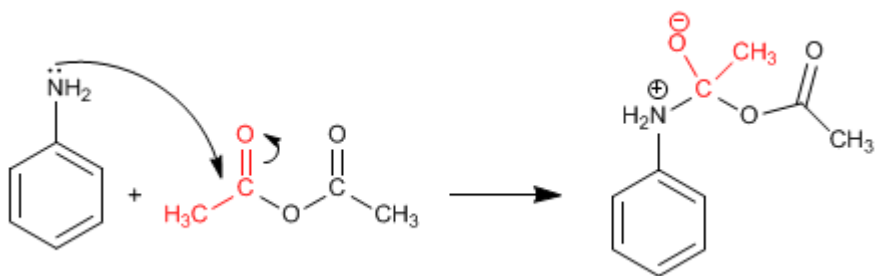


La protección del amino puede realizarse con anhídrido etanoico en piridina, o con cloruro de etanoilo en piridina

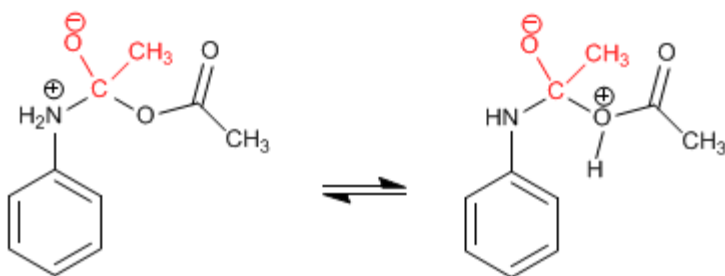


El producto final es una amida, mucho menos básica que la amina de partida y con menos tendencia a protonarse. El mecanismo de la reacción es el siguiente:

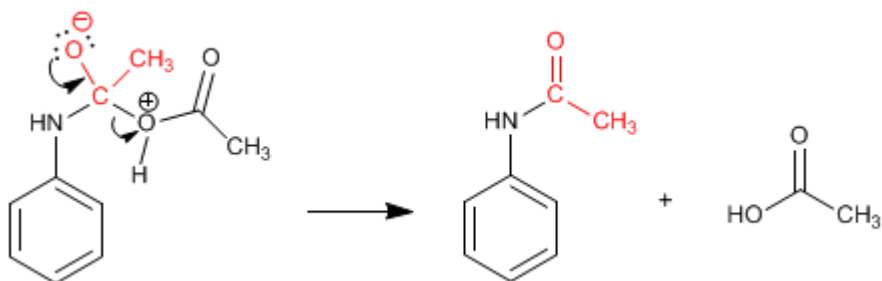
### Etapla 1. Adición



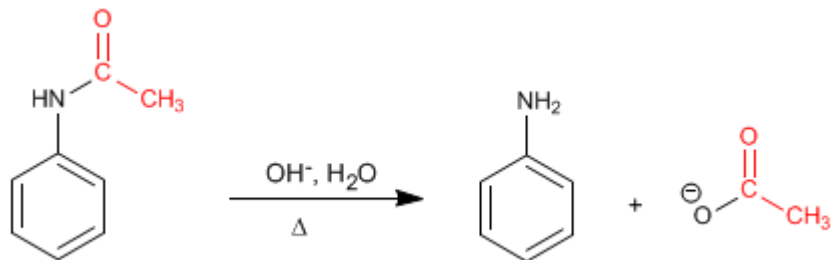
### Etapla 2. Equilibrio ácido-base



### Etapla 3. Eliminación



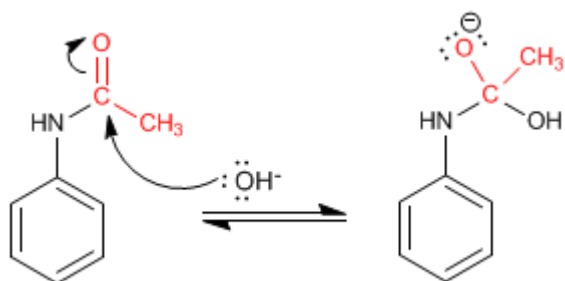
La amida formada se desprotege por hidrólisis ácida o básica, dejando libre la anilina.



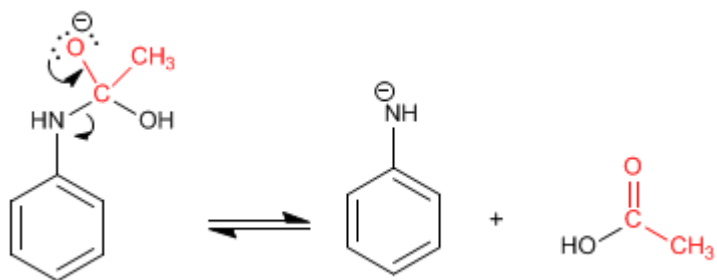
Mecanismo de desprotección en medio básico.



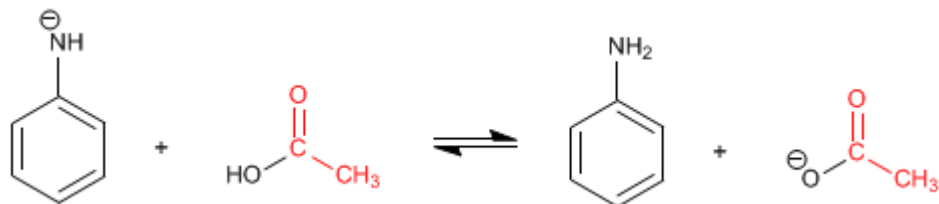
**Etapla 1.** Adición del grupo hidroxilo a la amida



**Etapla 2.** Eliminación

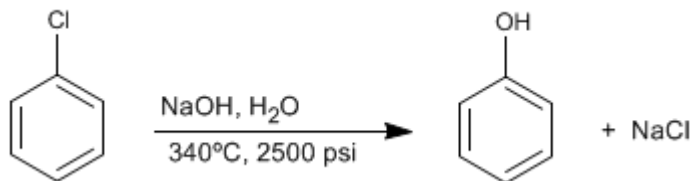


**Etapla 3.** Equilibrio ácido-base



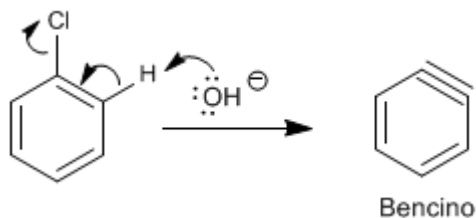
## Sustitución nucleófila aromática: Bencino

Los bencenos halogenados reaccionan con sosa diluida en condiciones de alta presión y temperatura, para formar fenoles. Esta reacción no requiere grupos desactivantes en posición orto/para y sigue un mecanismo diferente al de la sustitución nucleófila aromática por adición-eliminación.

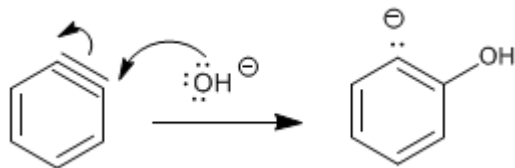


Esta reacción fue descubierta en 1928 por los químicos de la compañía Dow Chemical. El mecanismo consiste en la eliminación de HCl con formación de un intermedio inestable llamado bencino, el cual es atacado por los iones hidróxido del medio, para formar fenol.

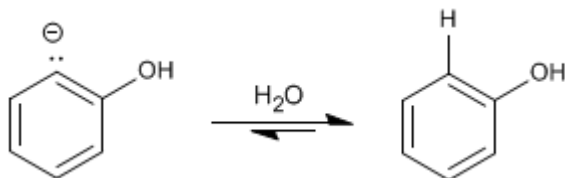
### Etapas 1. Eliminación de HCl



### Etapas 2. Adición del ion hidróxido al bencino



### Etapas 3. Protonación



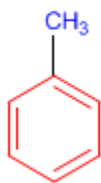
El mecanismo de esta reacción recibe el nombre de sustitución nucleófila aromática por eliminación-adición.

Cuando en el benceno existen sustituyentes produce mezclas, debido al ataque del nucleófilo sobre los dos carbonos del triple enlace.

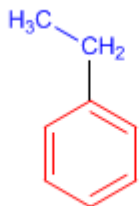
## PROBLEMAS NOMENCLATURA - BENCENO

### Nomenclatura de Benceno - Reglas IUPAC

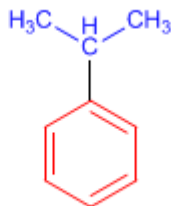
**Regla 1.** En bencenos monosustituídos, se nombra primero el radical y se termina en la palabra benceno.



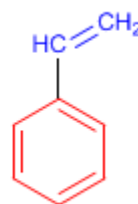
Metilbenceno



Etilbenceno



Isopropilbenceno



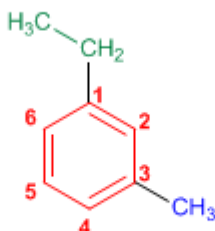
Vinilbenceno

**Regla 2.** En bencenos disustituídos se indica la posición de los radicales mediante los prefijos *orto-* (*o-*), *meta* (*m-*) y *para* (*p-*). También pueden emplearse los localizadores 1,2-, 1,3- y 1,4-.



*o*-Dimetilbenceno

(1,2-Dimetilbenceno)



*m*-Etilmetilbenceno

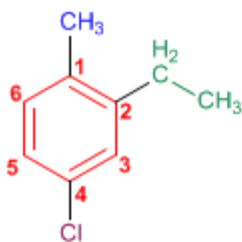
(1-Etil-3-metilbenceno)



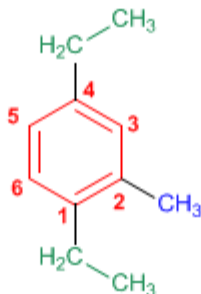
*p*-Isopropilmetilbenceno

(1-Isopropil-4-metilbenceno)

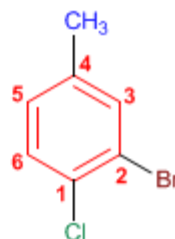
**Regla 3.** En bencenos con más de dos sustituyentes, se numera el anillo de modo que los sustituyentes tomen los menores localizadores. Si varias numeraciones dan los mismos localizadores se da preferencia al orden alfabético.



4-Cloro-2-etil-1-metilbenceno

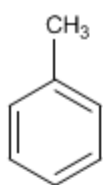


1,4-Dietil-2-metilbenceno

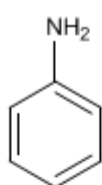


2-Bromo-1-cloro-4-metilbenceno

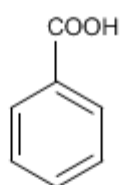
**Regla 4.** Existen numerosos derivados del benceno con nombres comunes que conviene saber:



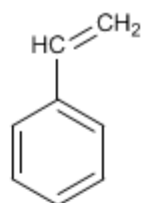
Tolueno



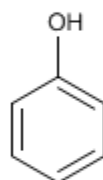
Anilina



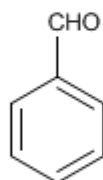
Ac. Benzoico



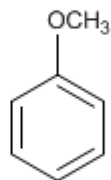
Estireno



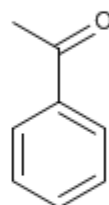
Fenol



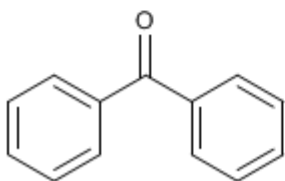
Benzaldehido



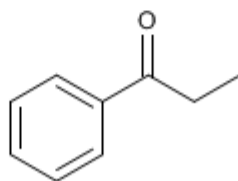
Anisol



Acetofenona



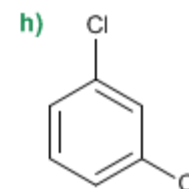
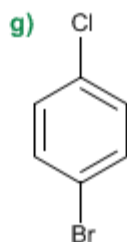
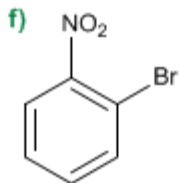
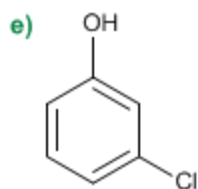
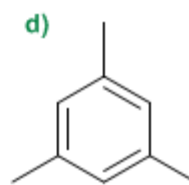
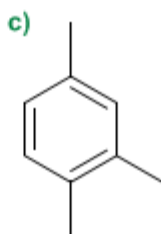
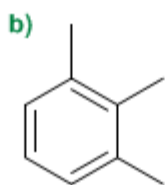
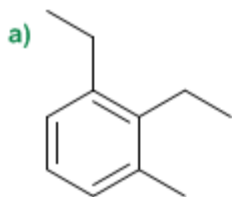
Benzofenona



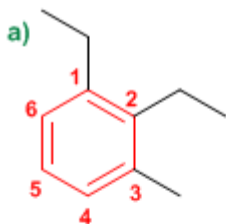
Propiofenona

## Nomenclatura de Benceno - Problema 0.1

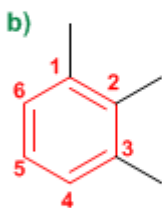
Nombra los siguientes derivados del benceno:



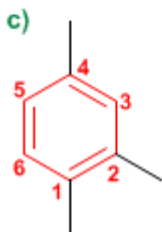
Solución



1. Cadena principal: benceno
2. Numeración: los sustituyentes deben tomar los menores localizadores, y además, se asignan los localizadores menores a los grupos que van antes en el orden alfabético (etilo antes que metilo)
3. Sustituyentes: etilos en 1,2 y metilo en 3.
4. Nombre: 1,2-Dietil-3-metilbenceno



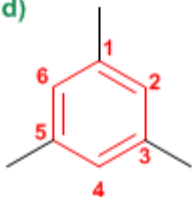
1. Cadena principal: benceno
2. Numeración: los sustituyentes deben tomar los menores localizadores.
3. Sustituyentes: metilos en posición 1,2,3.
4. Nombre: 1,2,3-Trimetilbenceno



1. Cadena principal: benceno
2. Numeración: los sustituyentes deben tomar los menores localizadores.
3. Sustituyentes: metilos en posición 1,2,4.
4. Nombre: 1,2,4-Trimetilbenceno

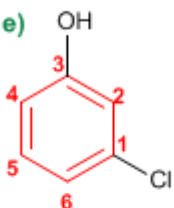
El anillo se numera para que los sustituyentes tomen los localizadores más bajos. En caso de empate se tiene en cuenta el orden alfabético

d)



1. Cadena principal: benceno
2. Numeración: se parte de un metilo y se numera en cualquier dirección.
3. Sustituyentes: metilos en 1,3,5.
4. Nombre: 1,3,5-Trimetilbenceno

e)



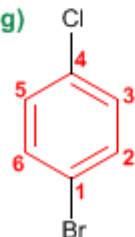
1. Cadena principal: benceno
2. Numeración: la numeración comienza en el cloro (va antes alfabéticamente) y prosigue por el camino más corto hacia el hidroxilo.
3. Sustituyentes: cloro en posición 1 e hidroxilo en posición 3 (posición meta)
4. Nombre: 1-Cloro-3-hidroxibenceno (*m*-Clorohidroxibenceno)

f)



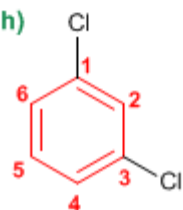
1. Cadena principal: benceno
2. Numeración: la numeración comienza en el bromo (preferencia alfabética)
3. Sustituyentes: bromo en posición 1 y nitro en posición 3 (posición orto)
4. Nombre: 1-Bromo-3-nitrobenzono (*o*-Bromonitrobenzono)

g)



1. Cadena principal: benceno
2. Numeración: comienza en el bromo (preferencia alfabética sobre el cloro)
3. Sustituyentes: bromo en 1 y cloro en 4 (posición para)
4. Nombre: 1-Bromo-4-clorobenceno (*p*-Bromoclorobenceno)

h)



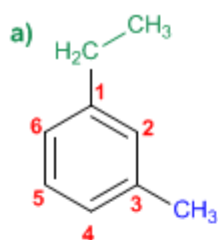
1. Cadena principal: benceno
2. Numeración: localizadores más bajos posibles a los cloros.
3. Sustituyentes: cloros en posición 1,3.
4. Nombre: 1,3-Diclorobenceno (*m*-Diclorobenceno)

## Nomenclatura de Benceno - Problema 0.2

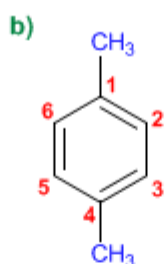
Formular los siguientes derivados del benceno:

- |   |   |
|---|---|
| a) 1-Etil-3-metilbenceno                | k) 4,5-Difenil-1-octeno                       |
| b) <i>p</i> -Dimetilbenceno             | l) 2-Fenil-4-metilhexeno                      |
| c) 1-Butil-3-etilbenceno                | m) 1-(metiletil)-4-(2-metilpropil)benceno     |
| d) <i>o</i> -Cloronitrobenceno          | n) 6-Fenil-3-metilhexa-1,4-dieno              |
| e) <i>m</i> -Bromoclorobenceno          | o) <i>cis</i> -1-Fenil-1-buteno               |
| f) <i>p</i> -Diisopropilbenceno         | p) <i>trans</i> -2-Fenil-2-buteno             |
| g) 1- <i>tert</i> -Butil-4-metilbenceno | q) 7-Etil-4,5-difenildec-5-en-1-ino           |
| h) <i>o</i> -Alilvinilbenceno           | r) <i>m</i> -Diciclohexilbenceno              |
| i) <i>m</i> -Etilpropilbenceno          | s) <i>p</i> -Ciclobutilciclobutilbenceno      |
| j) 2-Etil-1,4-dimetilbenceno            | t) 3-(1,1-Difeniletil)-3-metilhex-1-en-5-ino. |

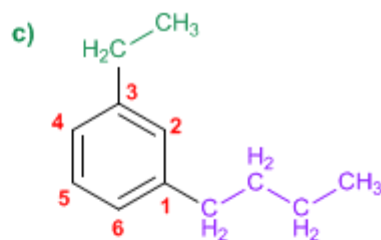
### Solución



1-Etil-3-metilbenceno



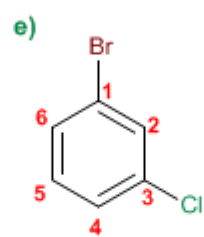
*p*-Dimetilbenceno



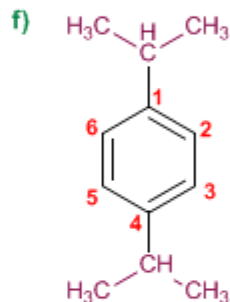
1-Butil-3-etilbenceno



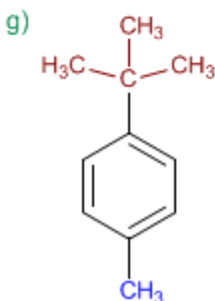
*o*-Cloronitrobenceno



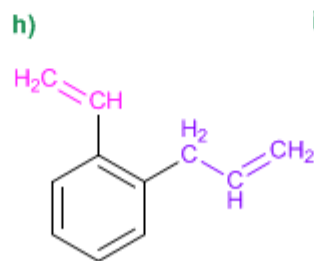
*m*-Bromoclorobenceno



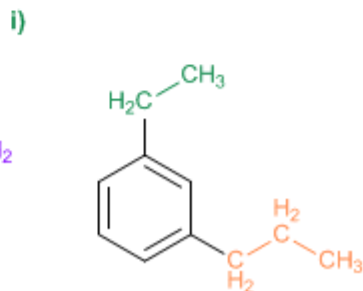
*p*-Diisopropilbenceno



1-*tert*-Butil-4-metilbenceno

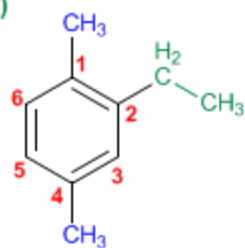


*o*-Alilvinilbenceno



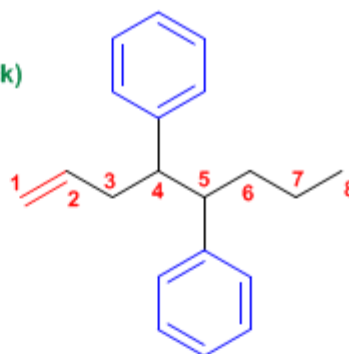
*m*-Etilpropilbenceno

j)



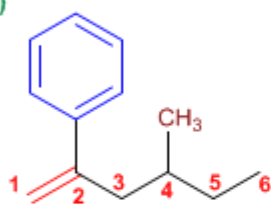
2-Etil-1,4-dimetilbenceno

k)



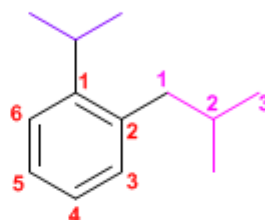
4,5-Difeniloct-1-eno

l)



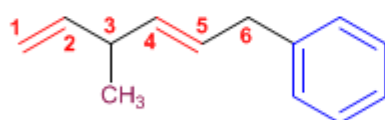
2-Fenil-4-metilhex-1-eno

m)



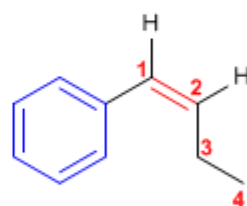
1-(metiletil)-2-(2-metilpropil)benceno

n)

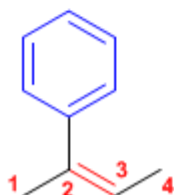


6-Fenil-3-metilhexa-1,4-dieno

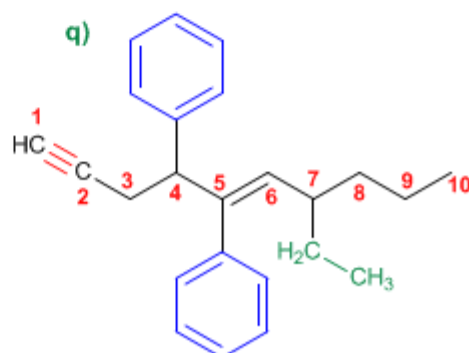
o)

*cis*-1-Fenil-1-butenó

p)

*trans*-2-Fenil-2-butenó

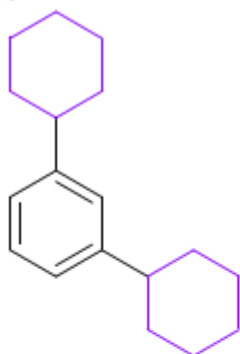
q)



7-Etil-4,5-difenildec-5-en-1-ino

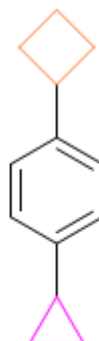


r)



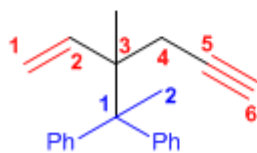
*m*-Diciclohexilbenceno

s)



*p*-Ciclobutilciclopropilbenceno

t)



3-(1,1-Difeniletil)-3-metilhex-1-en-5-ino.

## *Agradecimientos:*

❖ <http://www.quimicaorganica.org>

❖ <http://www.taringa.net/perfil/jose07070012>

5ª edición

# Química Orgánica



PEARSON  
Prentice  
Hall

L. C. Wade, Jr.

# ÍNDICE DE CONTENIDOS

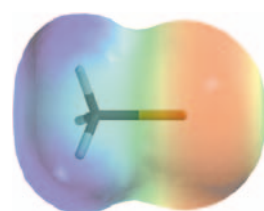
Prefacio xxii

Sobre el autor xxxvii

## Capítulo 1

### Introducción y revisión 1

- 1.1 Los orígenes de la química orgánica 1
- 1.2 Principios de la estructura atómica 3
- 1.3 La formación del enlace: la regla del octeto 6
- 1.4 Estructuras de Lewis 7
- 1.5 Enlace múltiple 8
  - Resumen: Modelos de enlace más frecuentes (sin carga) 9
- 1.6 La electronegatividad y la polaridad de enlace 9
- 1.7 Cargas formales 11
- 1.8 Estructuras iónicas 12
  - Resumen: Modelos de enlace más frecuentes en los compuestos e iones orgánicos 13
- 1.9 Resonancia 13
- 1.10 Fórmulas estructurales 17
- 1.11 Fórmulas moleculares y fórmulas empíricas 20
- 1.12 Ácidos y bases de Arrhenius 21
- 1.13 Ácidos y bases de Brønsted-Lowry 22
- 1.14 Ácidos y bases de Lewis 29
  - Glosario del Capítulo 1 32
  - Problemas 34

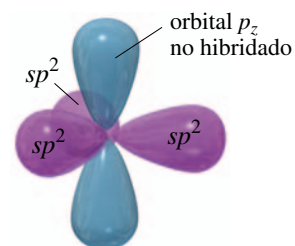


mapa del potencial electrostático del clorometano

## Capítulo 2

### Estructura y propiedades de las moléculas orgánicas 38

- 2.1 Propiedades ondulatorias de los electrones en los orbitales 38
- 2.2 Orbitales moleculares 40
- 2.3 Enlaces pi 43
- 2.4 Hibridación y geometría molecular 44
- 2.5 Representación de moléculas tridimensionales 47
- 2.6 Reglas generales de la hibridación y de la geometría 48
- 2.7 Rotación de enlaces 53
- 2.8 Isomería 54
- 2.9 Polaridad de enlaces y moléculas 57
- 2.10 Atracciones y repulsiones intermoleculares 60
- 2.11 Efecto de la polaridad en la solubilidad 64
- 2.12 Hidrocarburos 67
- 2.13 Compuestos orgánicos oxigenados 70
- 2.14 Compuestos orgánicos nitrogenados 72
  - Glosario del Capítulo 2 74
  - Problemas 76



átomo de carbono con hibridación  $sp^2$  (vista lateral)

## Capítulo 3

### Estructura y estereoquímica de los alcanos 80

- 3.1 Clasificación de los hidrocarburos (revisión) 80
- 3.2 Fórmulas moleculares de los alcanos 81
- 3.3 Nomenclatura de los alcanos 82  
Resumen: Reglas para la nomenclatura de los alcanos 87
- 3.4 Propiedades físicas de los alcanos 88
- 3.5 Aplicaciones y fuentes de los alcanos 90
- 3.6 Reacciones de los alcanos 92
- 3.7 Estructura y conformaciones de los alcanos 93
- 3.8 Conformaciones del butano 97
- 3.9 Conformaciones de los alcanos de cadena larga 99
- 3.10 Cicloalcanos 100
- 3.11 Isomería *cis-trans* en cicloalcanos 102
- 3.12 Estabilidad de los cicloalcanos: tensión de anillo 102
- 3.13 Conformaciones del ciclohexano 106  
*Estrategias para resolver problemas: Representación de las conformaciones de silla 109*
- 3.14 Conformaciones de ciclohexanos monosustituídos 110
- 3.15 Conformaciones de ciclohexanos disustituídos 113  
*Estrategias para resolver problemas: Reconocimiento de isómeros *cis* y *trans* 115*
- 3.16 Moléculas bicíclicas 117  
Glosario del Capítulo 3 118  
Problemas 122



## Capítulo 4

### El estudio de las reacciones químicas 124

- 4.1 Introducción 124
- 4.2 Cloración del metano 124
- 4.3 Reacción radicalaria en cadena 125  
**MECANISMO CLAVE: Halogenación radicalaria 127**
- 4.4 Constantes de equilibrio y energía libre 129
- 4.5 Entalpía y entropía 131
- 4.6 Energías de disociación de enlace 133
- 4.7 Variación de entalpía en la reacción de cloración 135
- 4.8 Cinética y ecuación de velocidad 136
- 4.9 Energía de activación e influencia de la temperatura en la velocidad de reacción 138
- 4.10 Estados de transición 140
- 4.11 Velocidades en reacciones de varias etapas 141
- 4.12 Influencia de la temperatura en la reacción de halogenación 142
- 4.13 Halogenación de alcanos superiores 143
- 4.14 El postulado de Hammond 149  
*Estrategias para resolver problemas: Propuesta de un mecanismo de reacción 151*
- 4.15 Inhibidores radicalarios 153
- 4.16 Intermedios reactivos 154  
Resumen: Intermedios reactivos 160  
Glosario del Capítulo 4 160  
Problemas 163

## Capítulo 5

### Estereoquímica 167

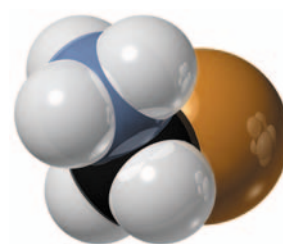
- 5.1 Introducción 167
- 5.2 Quiralidad 168
- 5.3 Nomenclatura (*R*) y (*S*) de átomos de carbono asimétricos 174
- 5.4 Actividad óptica 178
- 5.5 Discriminación biológica de los enantiómeros 183
- 5.6 Mezclas racémicas 184
- 5.7 Exceso enantiomérico y pureza óptica 186
- 5.8 Quiralidad de sistemas conformacionalmente móviles 187
- 5.9 Compuestos quirales sin átomos asimétricos 189
- 5.10 Proyecciones de Fischer 191
  - Resumen: Las proyecciones de Fischer y su uso 195
- 5.11 Diastereómeros o diastereoisómeros 195
  - Resumen: Tipos de isómeros 197
- 5.12 Estereoquímica de las moléculas con dos o más carbonos asimétricos 198
- 5.13 Compuestos *meso* 199
- 5.14 Configuración absoluta y relativa 201
- 5.15 Propiedades físicas de los diastereómeros 202
- 5.16 Resolución de enantiómeros 204
  - Glosario del Capítulo 5 207
  - Problemas 209



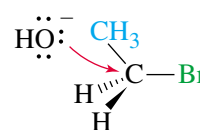
## Capítulo 6

### Haluros de alquilo: sustitución nucleofílica y eliminación 212

- 6.1 Introducción 212
- 6.2 Nomenclatura de haluros de alquilo 213
- 6.3 Aplicaciones y usos de los haluros de alquilo 215
- 6.4 Estructura de los haluros de alquilo 217
- 6.5 Propiedades físicas de los haluros de alquilo 218
- 6.6 Preparación de los haluros de alquilo 220
  - Resumen: Métodos de preparación de los haluros de alquilo 222
- 6.7 Reacciones de los haluros de alquilo: sustitución y eliminación 224
- 6.8 Sustitución nucleofílica bimolecular: la reacción  $S_N2$  225
  - MECANISMO CLAVE: La reacción  $S_N2$  225**
- 6.9 Generalidades sobre la reacción  $S_N2$  227
  - Resumen: Reacciones  $S_N2$  de haluros de alquilo 227
- 6.10 Factores que condicionan las reacciones  $S_N2$ : fuerza de los nucleófilos 228
  - Resumen: Tendencias en la nucleofilia 230
- 6.11 Reactividad del sustrato en las reacciones  $S_N2$  233
- 6.12 Estereoquímica de la reacción  $S_N2$  236
- 6.13 Sustitución nucleofílica unimolecular: la reacción  $S_N1$  238
  - MECANISMO CLAVE: La reacción  $S_N1$  239**
- 6.14 Estereoquímica de la reacción  $S_N1$  242
- 6.15 Reordenamientos en las reacciones  $S_N1$  243
- 6.16 Comparación de las reacciones  $S_N1$  y  $S_N2$  246
  - Resumen: Sustituciones nucleofílicas 247



bromuro de etilo ( $1^\circ$ )  
el ataque es fácil





- 6.17 Eliminación unimolecular: la reacción E1 248  
**MECANISMO CLAVE: La reacción E1 248**  
Resumen: Reacciones mediadas por carbocationes 251
- 6.18 Eliminación bimolecular: la reacción E2 252  
**MECANISMO CLAVE: La reacción E2 252**
- 6.19 Orientación en las reacciones de eliminación: la regla de Saytzeff 253
- 6.20 Estereoquímica de la reacción E2 255
- 6.21 Comparación de los mecanismos de eliminación E1 y E2 257  
Resumen: Reacciones de eliminación 258  
**Estrategias para resolver problemas: Predicción de los productos resultantes de las sustituciones y eliminaciones 259**  
Resumen: Reacciones de los haluros de alquilo 261  
Glosario del Capítulo 6 264  
Problemas 267

## Capítulo 7

### Estructura y síntesis de alquenos 272

- 7.1 Introducción 272
- 7.2 Descripción de los orbitales del doble enlace en los alquenos 272
- 7.3 Elementos de insaturación 274
- 7.4 Nomenclatura de los alquenos 276
- 7.5 Nomenclatura de los isómeros *cis-trans* 278  
Resumen: Reglas para nombrar los alquenos 280
- 7.6 Importancia comercial de los alquenos 281
- 7.7 Estabilidad de los alquenos 283
- 7.8 Propiedades físicas de los alquenos 289
- 7.9 Síntesis de alquenos mediante eliminación de haluros de alquilo 291
- 7.10 Síntesis de alquenos mediante deshidratación de alcoholes 300  
**MECANISMO CLAVE: Deshidratación de un alcohol catalizada por ácidos 300**
- 7.11 Métodos industriales de síntesis de alquenos a alta temperatura 301  
**Estrategias para resolver problemas: Propuesta de mecanismos de reacción 303**  
Resumen: Métodos de síntesis de alquenos 306  
Glosario del Capítulo 7 308  
Problemas 310



## Capítulo 8

### Reacción de alquenos 314

- 8.1 Reactividad del doble enlace carbono-carbono 314
- 8.2 Adición electrofílica a alquenos 315  
**MECANISMO CLAVE: Adición electrofílica a alquenos 315**
- 8.3 Adición de haluros de hidrógeno a alquenos 317
- 8.4 Adición de agua: hidratación de alquenos 322
- 8.5 Hidratación mediante oximercuriación-desmercuriación 324
- 8.6 Alcoximercuriación-desmercuriación 326
- 8.7 Hidroboración de alquenos 328
- 8.8 Hidrogenación catalítica de alquenos 333
- 8.9 Adición de carbenos a alquenos 336
- 8.10 Adición de halógenos a alquenos 338
- 8.11 Formación de halohidrinas 341
- 8.12 Epoxidación de alquenos 344
- 8.13 Apertura de epóxidos catalizada por ácidos 345
- 8.14 Hidroxilación de alquenos en *sin* 347
- 8.15 Ruptura oxidativa de alquenos 349

- 8.16 Polimerización de alquenos 352  
[Estrategias para resolver problemas: Síntesis orgánica](#) 357  
Resumen: Reacciones de alquenos 359  
Glosario del Capítulo 8 363  
Problemas 365

---

## Capítulo 9

### Alquinos 370

- 9.1 Introducción 370  
9.2 Nomenclatura de alquinos 371  
9.3 Propiedades físicas de los alquinos 372  
9.4 Importancia comercial de los alquinos 372  
9.5 Estructura electrónica de los alquinos 374  
9.6 Acidez de los alquinos 375  
9.7 Síntesis de alquinos a partir de acetiluros 378  
9.8 Síntesis de alquinos mediante reacciones de eliminación 382  
Resumen: Síntesis de alquinos 384  
9.9 Reacciones de adición a alquinos 385  
9.10 Reacciones de oxidación de alquinos 394  
[Estrategias para resolver problemas: Síntesis en varias etapas](#) 396  
Resumen: Reacciones de alquinos 397  
Glosario del Capítulo 9 400  
Problemas 401

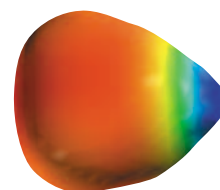


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## Capítulo 10

### Estructura y síntesis de alcoholes 405

- 10.1 Introducción 405  
10.2 Estructura y clasificación de los alcoholes 405  
10.3 Nomenclatura de los alcoholes y fenoles 407  
10.4 Propiedades físicas de los alcoholes 411  
10.5 Importancia comercial de los alcoholes 413  
10.6 Acidez de los alcoholes y fenoles 415  
10.7 Síntesis de alcoholes: introducción y revisión 418  
Resumen: Síntesis previas de alcoholes 418  
10.8 Reactivos organometálicos utilizados para la síntesis de alcoholes 420  
10.9 Adición de reactivos organometálicos a compuestos carbonílicos 422  
[MECANISMO CLAVE: Reacciones de Grignard](#) 423  
Resumen: Reacciones de Grignard 429  
10.10 Reacciones secundarias de compuestos organometálicos: reducción de haluros de alquilo 430  
10.11 Reducción del grupo carbonilo: síntesis de alcoholes primarios y secundarios 432  
Resumen: Reacciones de  $\text{LiAlH}_4$  y  $\text{NaBH}_4$  434  
Resumen: Síntesis de alcoholes 435  
10.12 Tioles (mercaptanos) 437  
Glosario del Capítulo 10 440  
Problemas 441



mapa de potencial  
electrostático del metililitio

---

## Capítulo 11

### Reacciones de alcoholes 445

- 11.1 Estados de oxidación de los alcoholes y de los grupos funcionales relacionados 445  
11.2 Oxidación de alcoholes 447  
11.3 Métodos adicionales de oxidación de alcoholes 450



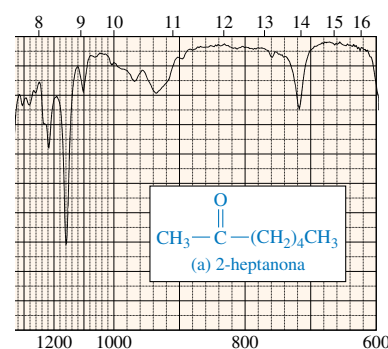
- 11.4 Oxidación biológica de alcoholes 452
- 11.5 Los alcoholes como nucleófilos y electrófilos: formación de tosilatos 454  
Resumen: Reacciones  $S_N2$  de tosilatos 456
- 11.6 Reducción de alcoholes 457
- 11.7 Reacciones de alcoholes con haluros de hidrógeno 457
- 11.8 Reacciones de alcoholes con haluros de fósforo 461
- 11.9 Reacciones de alcoholes con cloruro de tionilo 463
- 11.10 Reacciones de deshidratación de alcoholes 464  
**Estrategias para resolver problemas: Propuesta de mecanismos de reacción 468**
- 11.11 Reacciones características de los dioles 472
- 11.12 Esterificación de alcoholes 474
- 11.13 Ésteres de ácidos inorgánicos 475
- 11.14 Reacciones de los alcóxidos 477  
**MECANISMO CLAVE: Síntesis de Williamson de éteres 478**  
**Estrategias para resolver problemas: Síntesis en varias etapas 479**  
Resumen: Reacciones de alcoholes 482  
Glosario del Capítulo 11 485  
Problemas 486



## Capítulo 12

### Espectroscopía de infrarrojo y espectrometría de masas 490

- 12.1 Introducción 490
- 12.2 El espectro electromagnético 491
- 12.3 La región del infrarrojo 492
- 12.4 Vibraciones moleculares 493
- 12.5 Vibraciones activas e inactivas en el IR 495
- 12.6 Registro del espectro infrarrojo 496
- 12.7 Espectroscopía infrarroja de los hidrocarburos 499
- 12.8 Absorciones características de los alcoholes y las aminas 504
- 12.9 Absorciones características de los compuestos carbonílicos 505
- 12.10 Absorciones características de los enlaces C—N 511
- 12.11 Breve resumen de las frecuencias de tensión en el IR 513
- 12.12 Análisis e interpretación de los espectros de IR (problemas resueltos) 514
- 12.13 Introducción a la espectrometría de masas 519
- 12.14 Determinación de la fórmula molecular mediante espectrometría de masas 522
- 12.15 Modelos de fragmentación en la espectrometría de masas 526  
Resumen: Modelos comunes de fragmentación de masas 530  
Glosario del Capítulo 12 531  
Problemas 533

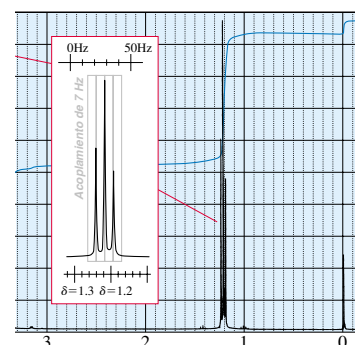


## Capítulo 13

### Espectroscopía de resonancia magnética nuclear 539

- 13.1 Introducción 539
- 13.2 Teoría de la resonancia magnética nuclear 539
- 13.3 Apantallamiento magnético por parte de los electrones 542
- 13.4 El espectrómetro de RMN 544
- 13.5 El desplazamiento químico 545
- 13.6 El número de señales 552
- 13.7 El área de los picos 553
- 13.8 Desdoblamiento espín-espín 556  
**Estrategias para resolver problemas: Representación de un espectro de RMN 561**

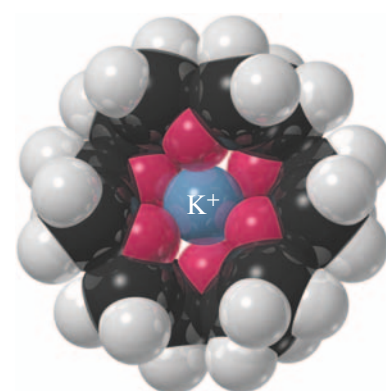
- 13.9 Acoplamientos complejos 565
- 13.10 Protones no equivalentes según la estequímica 568
- 13.11 Dependencia de la variable tiempo en la espectroscopía de RMN 571  
Estrategias para resolver problemas: Interpretación de un espectro de RMN de protón 574
- 13.12 Espectroscopía de RMN de carbono-13 579
- 13.13 Interpretación de un espectro de RMN de carbono 584
- 13.14 Imágenes mediante resonancia magnética nuclear 587  
Estrategias para resolver problemas: Problemas de espectroscopía 588
- Glosario del Capítulo 13 592
- Problemas 593



## Capítulo 14

### Éteres, epóxidos y sulfuros 600

- 14.1 Introducción 600
- 14.2 Propiedades físicas de los éteres 600
- 14.3 Nomenclatura de los éteres 605
- 14.4 Espectroscopía de los éteres 608
- 14.5 La síntesis de Williamson de éteres 610
- 14.6 Síntesis de éteres mediante alcoximercuriación-desmercuriación 612
- 14.7 Síntesis industrial: deshidratación bimolecular de alcoholes 612  
Resumen: Síntesis de éteres 613
- 14.8 Ruptura de éteres con HBr y HI 613
- 14.9 Autooxidación de éteres 615  
Resumen: Reacciones de éteres 616
- 14.10 Sulfuros (tioéteres) 616
- 14.11 Síntesis de epóxidos 619  
Resumen: Síntesis de epóxidos 622
- 14.12 Apertura de epóxidos catalizada por ácidos 622
- 14.13 Apertura de epóxidos catalizada por bases 625
- 14.14 Orientación en la apertura de epóxidos 627
- 14.15 Reacciones de epóxidos con reactivos de Grignard y compuestos organolíticos 629
- 14.16 Resinas epoxi: el advenimiento de los pegamentos modernos 629  
Resumen: Reacciones de epóxidos 631
- Glosario del Capítulo 14 632
- Problemas 634



éter 18-corona-6  
solvatando el  $K^+$

## Capítulo 15

### Sistemas conjugados, simetría orbital y espectroscopía ultravioleta 638

- 15.1 Introducción 638
- 15.2 Estabilidad de los dienos 638
- 15.3 Los sistemas conjugados según la teoría de orbitales moleculares 640
- 15.4 Los cationes alílicos 644
- 15.5 Adición 1,2 y 1,4 a dienos conjugados 645
- 15.6 Control cinético frente a control termodinámico en la adición de HBr a 1,3-butadieno 647
- 15.7 Radicales alílicos 649
- 15.8 Los orbitales moleculares del sistema alílico 651
- 15.9 Configuraciones electrónicas del radical, del catión y del anión alilo 652
- 15.10 Reacciones de sustitución  $S_N2$  de haluros de alilo y de tosilatos 654
- 15.11 La reacción de Diels-Alder 655



**MECANISMO CLAVE: La reacción de Diels-Alder 656**

- 15.12 La reacción de Diels-Alder como ejemplo de una reacción pericíclica 663
- 15.13 Espectroscopía de absorción ultravioleta 666
- Glosario del Capítulo 15 672
- Problemas 675

## Capítulo 16

### Compuestos aromáticos 679

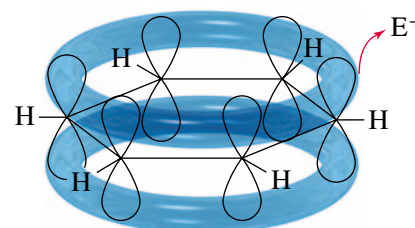
- 16.1 Introducción: el descubrimiento del benceno 679
- 16.2 Estructura y propiedades del benceno 679
- 16.3 Los orbitales moleculares del benceno 684
- 16.4 El ciclobutadieno según la teoría de orbitales moleculares 686
- 16.5 Compuestos aromáticos, antiaromáticos y no aromáticos 688
- 16.6 La regla de Hückel 689
- 16.7 Derivación de la regla de Hückel de la teoría de orbitales moleculares 691
- 16.8 Iones aromáticos 692
- 16.9 Compuestos aromáticos heterocíclicos 697
- 16.10 Hidrocarburos aromáticos polinucleares 702
- 16.11 Alótropos aromáticos del carbono 704
- 16.12 Compuestos heterocíclicos fusionados 706
- 16.13 Nomenclatura de los derivados del benceno 707
- 16.14 Propiedades físicas del benceno y de sus derivados 709
- 16.15 Espectroscopía de los compuestos aromáticos 710
- Glosario del Capítulo 16 713
- Problemas 715



## Capítulo 17

### Reacciones de compuestos aromáticos 722

- 17.1 Sustitución electrofílica aromática 722
- MECANISMO CLAVE: Sustitución electrofílica aromática 723**
- 17.2 Halogenación del benceno 723
- 17.3 Nitración del benceno 726
- 17.4 Sulfonación del benceno 726
- 17.5 Nitración del tolueno: efecto de la sustitución con grupos alquilo 728
- 17.6 Sustituyentes activadores *orto* y *para*-orientadores 730
- Resumen: Activadores *orto* y *para*-orientadores 733
- 17.7 Sustituyentes desactivadores *meta*-orientadores 734
- Resumen: Desactivadores *meta*-orientadores 737
- 17.8 Sustituyentes halogenados: desactivadores, pero *orto*, *para*-orientadores 737
- Resumen: Efectos orientadores de los sustituyentes 739
- 17.9 Efecto de múltiples sustituyentes sobre la sustitución electrofílica aromática 739
- 17.10 Alquilación de Friedel-Crafts 742
- 17.11 Acilación de Friedel-Crafts 746
- Resumen: Comparación de la alquilación y acilación de Friedel-Crafts 748
- 17.12 Sustitución nucleofílica aromática 750
- 17.13 Reacciones de adición de los derivados del benceno 754
- 17.14 Reacciones de las cadenas laterales de los derivados del benceno 757
- 17.15 Reacciones de los fenoles 761
- Resumen: Reacciones de los compuestos aromáticos 764
- Glosario del Capítulo 17 767
- Problemas 769



## Capítulo 18

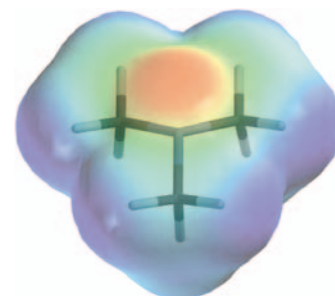
### Cetonas y aldehídos 774

- 18.1 Compuestos carbonílicos 774
- 18.2 Estructura del grupo carbonilo 775
- 18.3 Nomenclatura de cetonas y aldehídos 775
- 18.4 Propiedades físicas de cetonas y aldehídos 778
- 18.5 Espectroscopía de cetonas y aldehídos 780
- 18.6 Importancia industrial de cetonas y aldehídos 787
- 18.7 Revisión de la síntesis de cetonas y aldehídos 787
- 18.8 Síntesis de cetonas y aldehídos a partir de 1,3-ditianos 791
- 18.9 Síntesis de cetonas a partir de ácidos carboxílicos 792
- 18.10 Síntesis de cetonas a partir de nitrilos 793
- 18.11 Síntesis de aldehídos y cetonas a partir de cloruros de ácido 793  
Resumen: Síntesis de cetonas y aldehídos 795
- 18.12 Reacciones de cetonas y aldehídos: adición nucleofílica 797  
**MECANISMO CLAVE: Adiciones nucleofílicas a grupos carbonilo 800**
- 18.13 La reacción de Wittig 800
- 18.14 Hidratación de cetonas y aldehídos 804
- 18.15 Formación de cianohidrinas 806
- 18.16 Formación de iminas 807  
**MECANISMO CLAVE: Formación de iminas 808**
- 18.17 Condensaciones con hidroxilamina e hidrazinas 810  
Resumen: Condensación de aminas con cetonas y aldehídos 811
- 18.18 Formación de acetales 811  
**MECANISMO CLAVE: Formación de acetales 812**  
**Estrategias para resolver problemas: Propuesta de mecanismos de reacción 815**
- 18.19 El uso de acetales como grupos protectores 817
- 18.20 Oxidación de aldehídos 818
- 18.21 Otras reducciones de cetonas y aldehídos 819  
Resumen: Reacciones de cetonas y aldehídos 821  
Glosario del Capítulo 18 824  
Problemas 827

## Capítulo 19

### Aminas 836

- 19.1 Introducción 836
- 19.2 Nomenclatura de las aminas 837
- 19.3 Estructura de las aminas 839
- 19.4 Propiedades físicas de las aminas 841
- 19.5 Basicidad de las aminas 842
- 19.6 Efectos sobre la basicidad de las aminas 844
- 19.7 Sales de amonio 846
- 19.8 Sales de amonio y catalizadores de transferencia de fase 848
- 19.9 Espectroscopía de las aminas 849
- 19.10 Reacciones de las aminas con cetonas y aldehídos (revisión) 854
- 19.11 Sustitución aromática en arilaminas y piridina (revisión) 854
- 19.12 Alquilación de aminas con haluros de alquilo 858
- 19.13 Acilación de aminas con cloruros de ácido 859
- 19.14 Formación de sulfonamidas 861
- 19.15 Aminas como grupos salientes: la eliminación de Hofmann 862
- 19.16 Oxidación de aminas. La eliminación de Cope 865



mapa de potencial electrostático de la trimetilamina

- 19.17 Reacciones de aminas con ácido nitroso 868
- 19.18 Reacciones de las sales de diazonio aromáticas 870
- Resumen: Reacciones de las aminas 874
- 19.19 Síntesis de aminas 877
- Resumen: Síntesis de aminas 887
- Glosario del Capítulo 19 890
- Problemas 892

---

## Capítulo 20

### Ácidos carboxílicos 900

- 20.1 Introducción 900
- 20.2 Nomenclatura de los ácidos carboxílicos 900
- 20.3 Estructura y propiedades físicas de los ácidos carboxílicos 904
- 20.4 Acidez de los ácidos carboxílicos 906
- 20.5 Sales de ácidos carboxílicos 909
- 20.6 Fuentes comerciales de los ácidos carboxílicos 912
- 20.7 Espectroscopía de los ácidos carboxílicos 913
- 20.8 Síntesis de los ácidos carboxílicos 918
- Resumen: Síntesis de los ácidos carboxílicos 920
- 20.9 Reacciones de los ácidos carboxílicos y sus derivados. Sustitución nucleofílica en el grupo acilo 921
- 20.10 Condensación de los ácidos con los alcoholes: la esterificación de Fischer 922
- MECANISMO CLAVE: Esterificación de Fischer 923**
- 20.11 Síntesis y aplicaciones de los cloruros de ácido 925
- 20.12 Esterificación con diazometano 928
- 20.13 Condensación de ácidos con aminas: síntesis directa de amidas 928
- 20.14 Reducción de los ácidos carboxílicos 929
- 20.15 Alquilación de los ácidos carboxílicos para obtener cetonas 931
- Resumen: Reacciones de los ácidos carboxílicos 931
- Glosario del Capítulo 20 933
- Problemas 934

---

## Capítulo 21

### Derivados de los ácidos carboxílicos 940

- 21.1 Introducción 940
- 21.2 Estructura y nomenclatura de los derivados de ácido 941
- 21.3 Propiedades físicas de los derivados de ácidos carboxílicos 947
- 21.4 Espectroscopía de los derivados de ácidos carboxílicos 950
- 21.5 Interconversión entre los derivados de ácidos mediante sustitución nucleofílica en el grupo acilo 957
- MECANISMO CLAVE: Mecanismo de adición-eliminación en la sustitución nucleofílica en el grupo acilo 957**
- 21.6 Sustitución nucleofílica en el grupo acilo catalizada por ácidos 964
- Estrategias para resolver problemas: Propuestas de mecanismos de reacción 965**
- 21.7 Hidrólisis de los derivados de ácidos carboxílicos 968
- 21.8 Reducción de los derivados de ácidos 972
- 21.9 Reacciones de los derivados de ácidos con reactivos organometálicos 975
- 21.10 Resumen de la química de los cloruros de ácido 976
- 21.11 Resumen de la química de los anhídridos de ácido 978
- 21.12 Resumen de la química de los ésteres 981
- 21.13 Resumen de la química de las amidas 984
- 21.14 Resumen de la química de los nitrilos 987
- 21.15 Tioésteres 988



- 21.16 Ésteres y amidas del ácido carbónico 990
- Glosario del Capítulo 21 992
- Problemas 994

## Capítulo 22

### Sustituciones en alfa, y condensaciones de enoles y de iones enolato 1003

- 22.1 Introducción 1003
- 22.2 Enoles e iones enolato 1004
- 22.3 Halogenación en alfa de cetonas 1007
- 22.4 Bromación en alfa de ácidos: la reacción de HVZ (Hell-Volhard-Zelinsky) 1012
- 22.5 Alquilación de iones enolato 1013
- 22.6 Formación y alquilación de enaminas 1015
- 22.7 Condensación aldólica de cetonas y aldehídos 1017
- MECANISMO CLAVE: Condensación aldólica catalizada por una base 1018**
- 22.8 Deshidratación de aldoles 1020
- MECANISMO CLAVE: Deshidratación de un aldol 1021**
- 22.9 Condensaciones aldólicas cruzadas 1021
- Estrategias para resolver problemas: Propuesta de mecanismos de reacción 1022**
- 22.10 Ciclaciones aldólicas 1025
- 22.11 Diseño de síntesis utilizando condensaciones aldólicas 1026
- 22.12 La condensación de Claisen de ésteres 1027
- MECANISMO CLAVE: Condensación de Claisen 1028**
- 22.13 La condensación de Dieckmann: un tipo de ciclación de Claisen 1031
- 22.14 Condensaciones de Claisen cruzadas 1031
- 22.15 Síntesis empleando compuestos  $\beta$ -dicarbonílicos 1034
- 22.16 La síntesis malónica 1036
- 22.17 La síntesis acetilacética 1039
- 22.18 Adiciones conjugadas: la reacción de Michael 1042
- MECANISMO CLAVE: Adiciones 1,2 y 1,4 1043**
- 22.19 La anillación de Robinson 1046
- Estrategias para resolver problemas: Propuesta de mecanismos de reacción 1047**
- Resumen: Adiciones y condensaciones de enolatos 1049
- Glosario del Capítulo 22 1051
- Problemas 1052



## Capítulo 23

### Carbohidratos y ácidos nucleicos 1057

- 23.1 Introducción 1057
- 23.2 Clasificación de los hidratos de carbono 1058
- 23.3 Monosacáridos 1059
- 23.4 Diastereómeros *eritro* y *treo* 1062
- 23.5 Epímeros 1063
- 23.6 Estructura cíclica de los monosacáridos 1064
- 23.7 Anómeros de los monosacáridos. Mutarrotación 1068
- 23.8 Reacciones de los monosacáridos: reacciones secundarias en medio básico 1070
- 23.9 Reducción de los monosacáridos 1072
- 23.10 Oxidación de los monosacáridos. Los azúcares reductores 1073
- 23.11 Los azúcares no reductores: formación de glicósidos 1075
- 23.12 Formación de éteres y ésteres 1078
- 23.13 Reacciones con fenilhidrazina: formación de osazonas 1080
- 23.14 Acortamiento de la cadena: degradación de Ruff 1081

- 23.15 Alargamiento de la cadena: síntesis de Kiliani-Fischer 1081  
Resumen: Reacciones de los azúcares 1083
- 23.16 La prueba de Fischer de la configuración de la glucosa 1085
- 23.17 Determinación del tamaño del anillo. Escisión de azúcares con ácido peryódico 1088
- 23.18 Disacáridos 1090
- 23.19 Polisacáridos 1095
- 23.20 Ácidos nucleicos: introducción 1098
- 23.21 Ribonucleósidos y ribonucleótidos 1100
- 23.22 La estructura del ácido ribonucleico 1102
- 23.23 La desoxirribosa y la estructura del ácido desoxirribonucleico 1102
- 23.24 Funciones adicionales de los nucleótidos 1106  
Glosario del Capítulo 23 1108  
Problemas 1111

---

## Capítulo 24

### Aminoácidos, péptidos y proteínas 1114

- 24.1 Introducción 1114
- 24.2 Estructura y estereoquímica de los  $\alpha$ -aminoácidos 1115
- 24.3 Propiedades ácido-base de los aminoácidos 1119
- 24.4 Puntos isoeléctricos y electroforesis 1121
- 24.5 Síntesis de aminoácidos 1123  
Resumen: Síntesis de aminoácidos 1127
- 24.6 Resolución de los aminoácidos 1128
- 24.7 Reacciones de los aminoácidos 1129  
Resumen: Reacciones de aminoácidos 1131
- 24.8 Estructura y nomenclatura de péptidos y proteínas 1132
- 24.9 Determinación de la estructura de los péptidos 1136
- 24.10 Síntesis de péptidos en solución 1142
- 24.11 Síntesis de péptidos en fase sólida 1145
- 24.12 Clasificación de las proteínas 1151
- 24.13 Niveles de la estructura de las proteínas 1151
- 24.14 Desnaturalización de las proteínas 1154  
Glosario del Capítulo 24 1156  
Problemas 1158

---

## Capítulo 25

### Lípidos 1162

- 25.1 Introducción 1162
- 25.2 Ceras 1162
- 25.3 Triglicéridos 1163
- 25.4 Saponificación de grasas y aceites. Jabones y detergentes 1166
- 25.5 Fosfolípidos 1170
- 25.6 Esteroides 1171
- 25.7 Prostaglandinas 1174
- 25.8 Terpenos 1175  
Glosario del Capítulo 25 1179  
Problemas 1180



---

## Capítulo 26

### Polímeros sintéticos 1182

- 26.1 Introducción 1182
- 26.2 Polímeros de adición 1183
- 26.3 Estereoquímica de los polímeros 1189
- 26.4 Control estereoquímico de la polimerización. Catalizadores de Ziegler-Natta 1190
- 26.5 Gomas naturales y sintéticas 1190
- 26.6 Copolímeros de dos o más monómeros 1192
- 26.7 Condensación de polímeros 1192
- 26.8 Estructura y propiedades de los polímeros 1196
- Glosario del Capítulo 26 1198
- Problemas 1200

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## Apéndices

- 1A Posiciones de absorción de protones en RMN, en varios entornos estructurales 1204
- 1B Constantes de acoplamiento espín-espín 1205
- 1C Desplazamientos químicos de  $^{13}\text{C}$  en los compuestos orgánicos 1205
- 2A Grupos de frecuencias características en el infrarrojo 1206
- 2B Absorciones en el infrarrojo características de los grupos funcionales 1209
- 3 Las reglas de Woodward-Fieser para predecir los espectros del ultravioleta-visible 1211
- 4A Métodos y sugerencias para proponer mecanismos 1215
- 4B Sugerencias para desarrollar síntesis de varios pasos 1218
- 5 Valores de  $\text{p}K_{\text{a}}$  de compuestos representativos 1219

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## Esquemas de Mecanismos y Mecanismos clave

- CAPÍTULO 4 Halogenación vía radicales libres 127
- CAPÍTULO 6 Bromación alílica 221
  - La reacción  $\text{S}_{\text{N}}2$  225
  - Inversión de la configuración en las reacciones  $\text{S}_{\text{N}}2$  237
  - La reacción  $\text{S}_{\text{N}}1$  239
  - Racemización en las reacciones  $\text{S}_{\text{N}}1$  242
  - Transposición de hidruro en las reacciones  $\text{S}_{\text{N}}1$  244
  - Transposición de metilo en la reacción  $\text{S}_{\text{N}}1$  245
  - La reacción  $\text{E}1$  248
  - Reordenamientos en la reacción  $\text{E}1$  250
  - La reacción  $\text{E}2$  252
- CAPÍTULO 7 Deshidrohalogenación a través del mecanismo  $\text{E}2$  291
  - Estereoquímica de la reacción  $\text{E}2$  293
  - Dibromación  $\text{E}2$  en la formación de un dibromuro vecinal 297
  - Deshidratación de un alcohol catalizada por un ácido 300
- CAPÍTULO 8 Adición electrofílica a alquenos 315
  - Adición iónica de  $\text{HBr}$  a un alqueno 316
  - Adición radicalaria de  $\text{HBr}$  a un alqueno 319
  - Hidratación de un alqueno catalizada por ácidos 323



	Oximercuriación de un alqueno	325
	Hidroboración de un alqueno	329
	Oxidación de un trialquilborano	332
	Adición de halógenos a alquenos	339
	Formación de halohidrinas	341
	Epoxidación de alquenos	344
	Apertura de epóxidos catalizada por ácidos	345
CAPÍTULO 9	Reducción de un alquino con un metal en amoniaco líquido	388
	Tautomería ceto-enólica catalizada por ácidos	392
CAPÍTULO 10	Reacciones de Grignard	423
	Reducción de un grupo carbonilo con hidruros	432
CAPÍTULO 11	Reacción de un alcohol terciario con HBr ( $S_N1$ )	458
	Reacción de un alcohol primario con HBr ( $S_N2$ )	458
	Reacción de alcoholes con $PBr_3$	462
	Revisión: Deshidratación de un alcohol catalizada por un ácido	464
	La transposición pinacolínica	472
	La síntesis de Williamson de éteres	478
CAPÍTULO 14	Ruptura de un éter con HBr	614
	Apertura de un epóxido catalizada por ácidos	622
	Apertura de un epóxido catalizada por ácidos en una solución alcohólica	623
	Apertura de un epóxido catalizada por bases	626
CAPÍTULO 15	Adición 1,2 y 1,4 a dienos conjugados	646
	Bromación alílica radicalaria	649
	La reacción de Diels-Alder	656
CAPÍTULO 17	Sustitución electrofílica aromática	723
	Bromación de benceno	723
	Nitración de benceno	726
	Sulfonación de benceno	727
	Alquilación de Friedel-Crafts	743
	Acilación de Friedel-Crafts	747
	Sustitución nucleofílica aromática (adición-eliminación)	751
	Sustitución nucleofílica aromática	753
	La reducción de Birch	756
CAPÍTULO 18	Adiciones nucleofílicas al grupo carbonilo	800
	La reacción de Wittig	802
	Hidratación de cetonas y aldehídos	804
	Formación de cianohidrinas	806
	Formación de iminas	808
	Formación de acetales	812
	Reducción de Wolff-Kishner	821
CAPÍTULO 19	Sustitución electrofílica aromática de la piridina	856
	Sustitución nucleofílica aromática de la piridina	857
	Acilación de una amina con un cloruro de ácido	859
	Eliminación de Hofmann	863
	Eliminación de Cope de un óxido de amina	867
	Diazoación de una amina	868
	Transposición de Hofmann	886
CAPÍTULO 20	Sustitución nucleofílica sobre el grupo acilo de un éster	922
	Esterificación de Fischer	923
	Esterificación con diazometano	928

CAPÍTULO 21	Mecanismo de adición-eliminación en la sustitución nucleofílica en el grupo acilo 957
	Transformación de un cloruro de ácido en un anhídrido 959
	Transformación de un cloruro de ácido en un éster 960
	Transformación de un cloruro de ácido en una amida 960
	Transformación de un anhídrido de ácido en un éster 961
	Transformación de un anhídrido de ácido en una amida 961
	Transformación de un éster en una amida (amonólisis de un éster) 962
	Transesterificación 967
	Saponificación de un éster 968
	Hidrólisis de una amida en medio básico 970
	Hidrólisis de una amida en medio ácido 971
	Hidrólisis catalizada por una base de un nitrilo 972
	Reducción de un éster por un hidruro 973
	Reacción de un éster con dos moles de un reactivo de Grignard 975
CAPÍTULO 22	Sustitución en alfa 1003
	Adición de un enolato a cetonas y aldehídos (condensación) 1003
	Sustitución de un enolato en un éster (condensación) 1004
	Tautomería ceto-enólica catalizada por una base 1004
	Tautomería ceto-enólica catalizada por un ácido 1005
	Halogenación promovida por una base 1008
	Pasos finales de la reacción del haloformo 1009
	Halogenación catalizada por un ácido 1011
	Condensación aldólica catalizada por una base 1018
	Condensación aldólica catalizada por un ácido 1020
	Deshidratación de un aldol 1021
	Condensación de Claisen 1028
	Adiciones 1,2 y 1,4 1043
CAPÍTULO 23	Formación de un hemiacetal cíclico 1064
	Epimerización de la glucosa catalizada por una base 1071
	Reordenamientos enodiol catalizados por una base 1072
CAPÍTULO 26	Polimerización radicalaria 1185
	Polimerización catiónica 1186
	Polimerización aniónica 1188

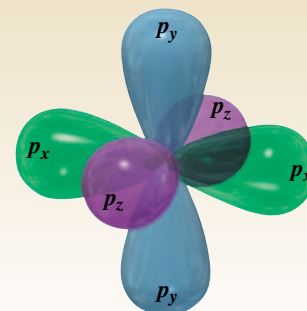
**Soluciones de los problemas seleccionados A1**

**Créditos de las fotografías CF1**

**Índice I1**

# CAPÍTULO 1

## Introducción y revisión



La definición moderna de **química orgánica** es la *química de los compuestos de carbono*. ¿Qué tiene de especial el carbono que hay una rama de la química que se dedica a él? Al contrario que otros elementos, el carbono forma enlaces fuertes con otros átomos de carbono y con una gran variedad de otros elementos. Las cadenas y anillos de átomos de carbono son tan variadas que se puede formar una variedad interminable de moléculas. Esta diversidad de los compuestos de carbono es la base para la vida en la Tierra. Los seres vivos están formados de compuestos orgánicos complejos con funciones estructurales, químicas o genéticas.

El término **orgánico** literalmente significa «derivado de los organismos vivos». Originalmente, la ciencia de la química orgánica era el estudio de los compuestos que se extraían de los organismos vivos o productos naturales. Compuestos tales como azúcar, urea, levadura, ceras y aceites vegetales eran considerados «orgánicos» y se aceptó el **Vitalismo** como teoría que explicaba su origen: la creencia en que los productos naturales necesitaban una «fuerza vital» para ser creados. Por tanto, la química orgánica era el estudio de los compuestos que tenían esa fuerza vital. La química inorgánica era el estudio de los gases, rocas, minerales y de los compuestos que se podían obtener a partir de ellos.

En el siglo XIX, la experimentación demostró que los compuestos orgánicos se podían sintetizar a partir de compuestos inorgánicos. En 1828, el químico alemán Friedrich Wöhler convirtió el cianato de amonio, obtenido a partir de amoníaco y ácido ciánico, en urea simplemente calentando el cianato en ausencia de oxígeno.



La urea también proviene de los seres vivos y se creía que contenía la fuerza vital, a pesar de que el cianato de amonio es inorgánico y por tanto, según aquella creencia, no poseía la fuerza vital. Algunos químicos sostenían que esa fuerza vital provenía de las manos de Wöhler, pero la mayoría reconocieron la posibilidad de sintetizar compuestos orgánicos a partir de compuestos inorgánicos. También se llevaron a cabo otras síntesis, por lo que la teoría de la fuerza vital se descartó.

Desde que el Vitalismo se descartó a comienzos del siglo XIX, se podría pensar que esta idea habría ya desaparecido, pero estaríamos equivocados, ya que el Vitalismo hoy forma parte de la mentalidad de las personas que creen que los productos «naturales» (derivados de las plantas) son diferentes y más saludables que aquellos compuestos exactamente iguales, «artificiales», que han sido sintetizados.

Como químicos, sabemos que los compuestos derivados de las plantas y los compuestos sintetizados son idénticos. La única diferencia es el contenido en  $^{14}\text{C}$ : los compuestos sintetizados a partir de derivados del petróleo tienen menor contenido del isótopo radioactivo  $^{14}\text{C}$ ,

### 1.1

## Los orígenes de la química orgánica



El corazón artificial Jarvik 7 está compuesto en gran parte de materiales orgánicos sintéticos.

ya que este isótopo ha ido desapareciendo con el tiempo. Los compuestos derivados de las plantas, al haber sido sintetizados recientemente a partir del  $\text{CO}_2$  del aire, tienen un contenido más elevado en  $^{14}\text{C}$ . Algunos suministradores importantes de productos químicos dan los análisis de los isótopos para confirmar que los «productos naturales» que distribuyen tienen mayor contenido en  $^{14}\text{C}$  y son derivados de las plantas. Estos sofisticados análisis dan un aspecto de alta tecnología al Vitalismo del siglo XXI.

A pesar de que los compuestos orgánicos no necesitan una fuerza vital, todavía se diferencian de los compuestos inorgánicos. La característica que distingue a los compuestos orgánicos es que *todos* contienen uno o más átomos de carbono. Pero no todos los compuestos que contienen carbono son orgánicos, sustancias tales como: diamante, grafito, dióxido de carbono, cianato de amonio y carbonato de sodio son compuestos derivados de minerales, y tienen propiedades características de los compuestos inorgánicos. No obstante, la mayoría de los millones de compuestos que contienen carbono se clasifican como orgánicos.

Nosotros mismos estamos compuestos en gran parte por moléculas orgánicas y nos alimentamos de compuestos orgánicos. Las proteínas de nuestra piel, los lípidos de las membranas de nuestras células, el glucógeno de nuestro hígado y el DNA del núcleo de nuestras células son compuestos orgánicos. Nuestros cuerpos también están regulados y son defendidos por compuestos orgánicos complejos.

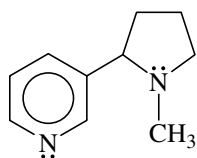
Los químicos han aprendido a diseñar y sintetizar muchas de estas moléculas complejas. Los productos sintéticos se utilizan como productos farmacéuticos, plásticos, pesticidas, pinturas y fibras. La mayoría de los avances más importantes en medicina se debe actualmente a los avances en química orgánica. Así, se sintetizan nuevos productos farmacéuticos para combatir enfermedades y se obtienen nuevos polímeros para elaborar dispositivos ortopédicos con los que sustituir órganos dañados. La química orgánica ha cerrado el ciclo, comenzó con el estudio de los compuestos derivados de «órganos» y ahora nos proporciona los productos farmacéuticos y materiales que necesitamos para salvar o reemplazar esos órganos.

Uno de los efectos de la nicotina es incrementar la concentración de una sustancia química en el sistema de estímulos cerebrales. La liberación de esta sustancia química hace que los fumadores se sientan bien y refuerza la necesidad de fumar.

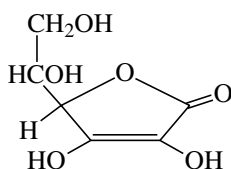
Una de las razones por las que los químicos sintetizan derivados de compuestos orgánicos complejos como la morfina es descubrir nuevas sustancias que mantengan sus propiedades útiles (analgesia) pero no las propiedades indeseables (adicción).



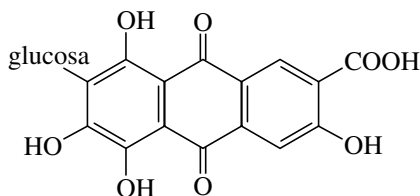
nicotina



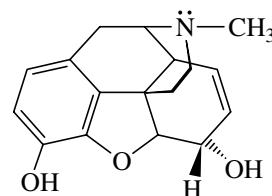
vitamina C



carmín



morfina



A continuación daré cuatro ejemplos de compuestos orgánicos aislados de organismos vivos: el tabaco contiene nicotina, un alcaloide que crea adicción; los escaramujos contienen vitamina C, esencial para prevenir el escorbuto; el carmín proviene de las cochinillas, insectos que suelen estar en las chumberas, y las adormideras contienen morfina, sustancia que mitiga el dolor pero provoca adicción.

Antes de comenzar el estudio de la química orgánica, se han de revisar algunos principios básicos. Muchos de los conceptos de estructura atómica y molecular son cruciales para entender la estructura y el enlace de los compuestos orgánicos.

### 1.2A Estructura del átomo

Los átomos están formados por protones, neutrones y electrones. Los protones están cargados positivamente y se encuentran, junto con los neutrones (sin carga), en el núcleo. Los electrones contienen una carga negativa de la misma magnitud que la carga positiva de los protones y se encuentran en el espacio que rodea al núcleo (Figura 1.1). Los protones y los neutrones tienen una masa parecida, aproximadamente unas 1800 veces la masa de un electrón. A pesar de que prácticamente toda la masa del átomo está concentrada en el núcleo, son los electrones los que participan en los enlaces químicos y en las reacciones.

Cada elemento se caracteriza por el número de protones que tiene en el núcleo (número atómico). El número de neutrones normalmente es parecido al número de protones, pero este número de neutrones puede variar. Los átomos que tienen el mismo número de protones pero diferente número de neutrones se llaman **isótopos**. Por ejemplo, el átomo de carbono más común es el que tiene seis protones y seis neutrones en el núcleo; su número másico (suma de protones y de neutrones) es 12, por lo que lo escribimos con el símbolo  $^{12}\text{C}$ . Aproximadamente el 1% de los átomos de carbono tienen 7 neutrones y su número másico es 13, simbolizado por  $^{13}\text{C}$ . Una fracción muy pequeña de átomos de carbono tiene ocho neutrones, por lo que su número másico es 14. El  $^{14}\text{C}$  es un isótopo radioactivo, con un periodo de semidesintegración (tiempo que tarda una determinada masa de ese isótopo en desintegrarse y perder la mitad de su masa) de 5 730 años. Este tiempo de desintegración del  $^{14}\text{C}$  se utiliza para determinar la edad de los materiales orgánicos de hasta unos 50 000 años de antigüedad.

### 1.2B Estructura electrónica del átomo

Las propiedades químicas de un elemento se determinan por el número de protones de su núcleo y el correspondiente número de electrones que hay alrededor del núcleo. Los electrones forman enlaces y determinan la estructura de las moléculas resultantes. Debido a que los electrones son muy pequeños y están en movimiento, se comportan simultáneamente como partículas y como ondas.

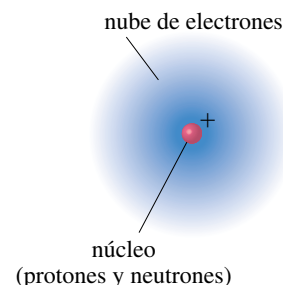
Los electrones que se encuentran moviéndose alrededor del núcleo se encuentran en **orbitales**. El principio de incertidumbre de Heisenberg dice que nunca se puede determinar con exactitud dónde se encuentra el electrón; sin embargo, se puede determinar la **densidad electrónica**, la probabilidad de encontrar al electrón en una determinada zona del orbital. Por tanto, un orbital es un estado de energía permitido para un electrón, con una función de probabilidad asociada que define la distribución de la densidad electrónica en el espacio.

Los orbitales atómicos se agrupan en «capas» o niveles diferentes a distintas distancias del núcleo. Cada capa se identifica por un número cuántico principal  $n$ , siendo  $n = 1$  para la capa de menor energía (la que está más próxima al núcleo). Al aumentar  $n$ , las capas están más alejadas del núcleo, tienen una energía más alta y pueden contener más electrones. La mayoría de los elementos más comunes de los compuestos orgánicos se encuentran en las dos primeras filas (periodos) de la tabla periódica, lo que indica que sus electrones se encuentran en las dos primeras capas de electrones. La primera capa ( $n = 1$ ) puede alojar dos electrones y la segunda capa ( $n = 2$ ) puede alojar ocho.

La primera capa de electrones contiene solamente el orbital  $1s$ . Todos los orbitales  $s$  tienen simetría esférica, lo cual quiere decir que son no direccionales. La densidad electrónica del orbital  $1s$  se representa en la Figura 1.2. Se puede observar que la densidad electrónica es más alta en las proximidades del núcleo y va disminuyendo exponencialmente según va aumentando la distancia al núcleo. Se podría comparar el orbital  $1s$  con una cápsula de algodón, donde la semilla representaría el núcleo. La densidad del algodón es mayor en los lugares próximos a la semilla y su densidad va disminuyendo según se va alejando del núcleo.

La segunda capa de electrones consta de orbitales  $2s$  y  $2p$ . El orbital  $2s$  posee simetría esférica igual que el  $1s$ , pero su densidad electrónica no es una simple función exponencial. El orbital  $2s$  tiene una densidad electrónica más pequeña en las proximidades del

## 1.2 Principios de la estructura atómica



▲ Figura 1.1

El átomo tiene un denso núcleo, cargado positivamente, rodeado de una nube de electrones.



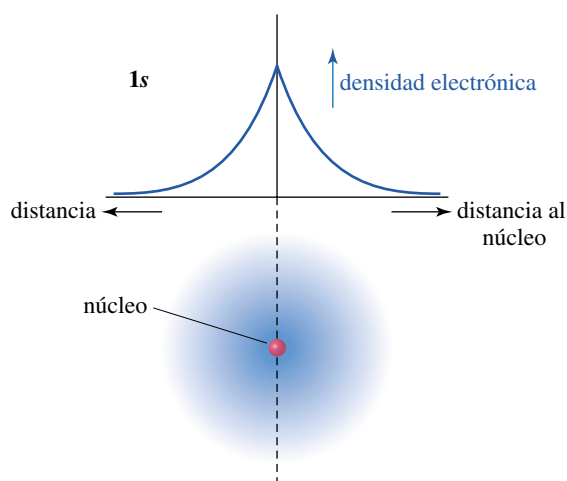
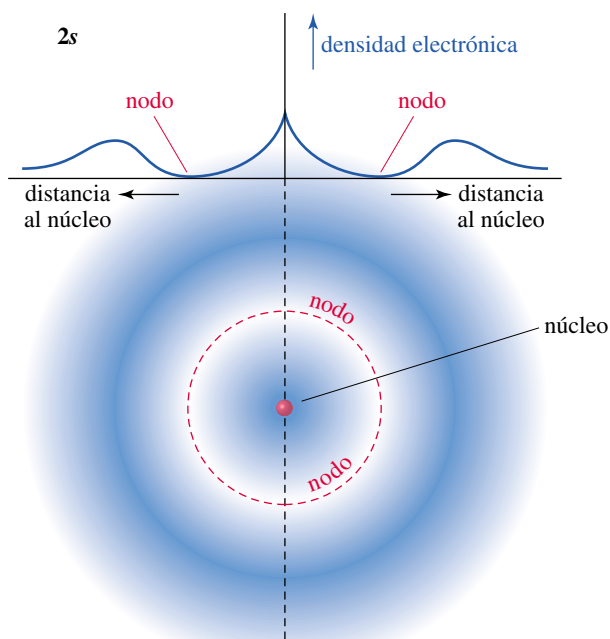
► **Figura 1.2**

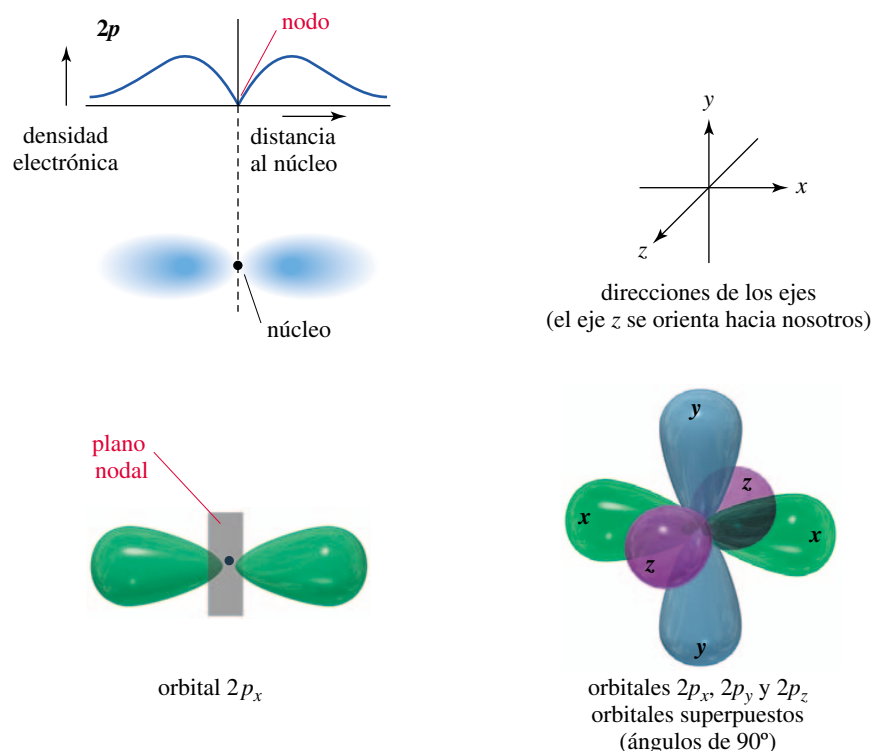
Gráfico y diagrama del orbital atómico 1s. La densidad electrónica es más alta cerca del núcleo y disminuye exponencialmente al aumentar la distancia al núcleo en cualquier dirección.

núcleo, ya que la mayor parte de la densidad electrónica está más alejada, más allá de una zona de densidad electrónica nula llamada **nodo**. Como la densidad electrónica del orbital 2s cerca del núcleo es menor que en el caso del orbital 1s, el orbital 2s tiene energía más alta. La Figura 1.3 muestra una representación gráfica del orbital 2s.

Además del orbital 2s, la segunda capa también contiene tres orbitales atómicos 2p, orientados cada uno de ellos en las tres direcciones del espacio. Estos tres orbitales reciben el nombre  $2p_x$ ,  $2p_y$  y  $2p_z$ , según su orientación a lo largo de los ejes  $x$ ,  $y$  o  $z$ . Los orbitales 2p tienen una energía ligeramente superior a la de los orbitales 2s, debido a que la localización media de los electrones en los orbitales 2p se sitúa a una distancia más alejada del núcleo. Cada orbital  $p$  consta de dos lóbulos, uno a cada lado del núcleo, con un **plano nodal** en el núcleo. El plano nodal es una región (plana) del espacio que incluye el núcleo y tiene una densidad electrónica nula. Los tres orbitales 2p únicamente difieren en sus orientaciones espaciales, por lo que tienen la misma energía. Los orbitales que tienen la misma cantidad de energía reciben el nombre de **orbitales degenerados**. La Figura 1.4 muestra las formas de los tres orbitales atómicos 2p degenerados.

► **Figura 1.3**

Los orbitales 2s tienen una pequeña región de densidad electrónica elevada próxima al núcleo, pero la mayor parte de la densidad electrónica está alejada del núcleo, más allá del nodo o región de densidad electrónica cero.



◀ **Figura 1.4**

Orbitales  $2p$ . Hay tres orbitales  $2p$ , orientados unos con respecto a los otros perpendicularmente. Se nombran según su orientación a lo largo del eje  $x$ ,  $y$  o  $z$ .

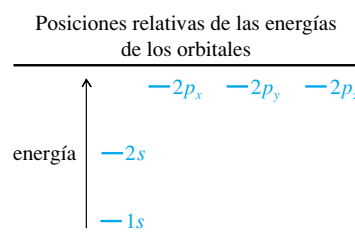
El *principio de exclusión de Pauli* dice que un orbital como máximo puede alojar dos electrones, de forma que sus espines estén apareados. La primera capa (un orbital  $1s$ ) puede alojar dos electrones. La segunda capa (un orbital  $2s$  y tres orbitales  $2p$ ) puede alojar ocho electrones y la tercera capa (un orbital  $3s$ , tres orbitales  $3p$  y cinco orbitales  $3d$ ) puede alojar 18 electrones.

## 1.2C Configuraciones electrónicas de los átomos

*Aufbau* significa «construir» en alemán, y el *principio de aufbau* explica cómo establecer la configuración electrónica de un átomo en su estado fundamental (el de mayor estabilidad). Se comienza con el orbital de energía más baja y se van llenando ordenadamente de menor a mayor energía hasta que se han colocado todos los electrones. La Tabla 1.1 muestra las configuraciones electrónicas en estado fundamental de todos los elementos que forman parte de los dos primeros periodos de la tabla periódica.

**TABLA 1.1** Configuraciones electrónicas de los elementos del primer y segundo periodo

Elemento	Configuración	Electrones de valencia
H	$1s^1$	1
He	$1s^2$	2
Li	$1s^2 2s^1$	1
Be	$1s^2 2s^2$	2
B	$1s^2 2s^2 2p_x^1$	3
C	$1s^2 2s^2 2p_x^1 2p_y^1$	4
N	$1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$	5
O	$1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$	6
F	$1s^2 2s^2 2p_x^2 2p_y^2 2p_z^1$	7
Ne	$1s^2 2s^2 2p_x^2 2p_y^2 2p_z^2$	8



► **Figura 1.5**

Primeras tres filas de la tabla periódica. La organización de la tabla periódica se debe al alojamiento de los electrones en los orbitales por orden creciente de energía. Para estos elementos representativos, el número de la columna corresponde al número de electrones de valencia.

**El carbonato de litio, una sal de litio, es un antidepresivo que se utiliza para tratar el problema psiquiátrico conocido como manía. La manía está caracterizada por comportamientos tales como alteraciones del humor, sentimientos de grandeza, obsesiones y dificultad para dormir. No se sabe cómo actúa el carbonato de litio cuando estabiliza el humor de este tipo de pacientes.**

Detalle de la tabla periódica

IA							gases nobles (VIII)
H	IIA	IIIA	IVA	VA	VIA	VIIA	He
Li	Be	B	C	N	O	F	Ne
Na	Mg	Al	Si	P	S	Cl	Ar

En la Tabla 1.1 se ilustran dos conceptos adicionales. Los **electrones de valencia** son los electrones que se encuentran en la capa más externa. El carbono tiene cuatro electrones de valencia, el nitrógeno cinco y el oxígeno seis. El helio tiene dos electrones de valencia y el neón tiene ocho, lo que corresponde, respectivamente, a la primera capa de valencia y a la segunda capa de valencia llenas. En general (para los elementos representativos), la columna o número de grupo de la tabla periódica corresponde al número de electrones de valencia (Figura 1.5). El hidrógeno y el litio tienen un electrón de valencia y los dos se encuentran en la primera columna (grupo IA) de la tabla periódica. El carbono tiene cuatro electrones de valencia y está en el grupo IVA de la tabla periódica.

Observad en la Tabla 1.1 que los electrones de valencia tercero y cuarto del carbono no están apareados, ocupan orbitales separados. A pesar de que el principio de exclusión de Pauli dice que dos electrones pueden ocupar el mismo orbital, los electrones se repelen uno a otro, y el apareamiento requiere energía adicional. La **regla de Hund** afirma que cuando hay dos o más orbitales de la misma energía, los electrones preferentemente se alojan en orbitales *diferentes* antes que aparearse en un mismo orbital. El primer electrón  $2p$  (caso del boro) se coloca en un orbital  $2p$ , el segundo (caso del carbono) en un orbital diferente y el tercero (caso del nitrógeno) se coloca en el último orbital  $2p$ . El cuarto, quinto y sexto electrón  $2p$  se aparearán, respectivamente, con los tres primeros electrones.

**PROBLEMA 1.1**

Escriba las configuraciones electrónicas de los elementos de la tercera fila que se muestra en la tabla periódica parcial de la Figura 1.5

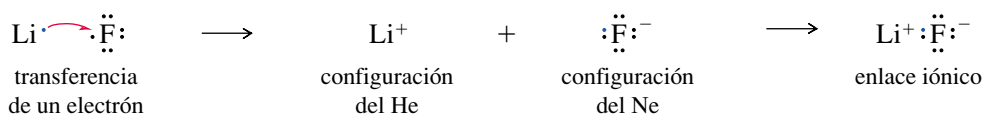
## 1.3

### La formación del enlace: la regla del octeto

En 1915, G. N. Lewis propuso varias teorías nuevas para describir cómo se enlazaban los átomos unos a otros para formar moléculas. Una de esas teorías afirma que una capa llena de electrones es especialmente estable y que *los átomos transfieren o comparten electrones para que de esa forma las capas se llenen de electrones*. Una capa llena de electrones tiene la configuración de un gas noble como el He, Ne o Ar. A este principio se le dio el nombre de la **regla del octeto** porque una capa llena implica ocho electrones de valencia para los elementos de la segunda fila de la tabla periódica.

**1.3A Enlace iónico**

Hay dos formas en las que los átomos pueden interactuar para adquirir configuraciones de gas noble. Algunas veces los átomos adquieren configuraciones de gas noble transfiriendo electrones de un átomo a otro. Por ejemplo, el litio tiene un electrón más en su configuración que el helio, y el fluor tiene un electrón menos que la configuración del neón; el litio pierde fácilmente sus electrones de valencia y el fluor los gana fácilmente:

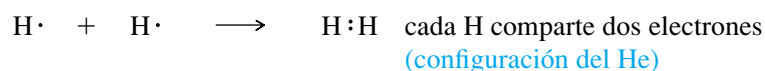




La transferencia de un electrón da a cada uno de los elementos la configuración de gas noble. Los iones resultantes tienen cargas opuestas y se atraen uno a otro formando un **enlace iónico**. El enlace iónico normalmente da lugar a la formación de grandes estructuras cristalinas en vez de moléculas individuales. El enlace iónico es muy frecuente en los compuestos inorgánicos, pero bastante inusual en los orgánicos.

### 1.3B Enlace covalente

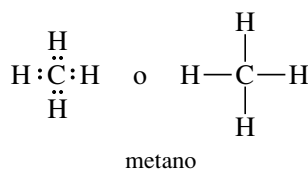
El **enlace covalente**, en el que se comparten electrones en lugar de transferirse, es la forma más habitual de enlace en los compuestos orgánicos. El hidrógeno, por ejemplo, necesita un segundo electrón para conseguir la configuración del gas noble helio. Si dos átomos de hidrógeno se unen y forman un enlace, «comparten» sus dos electrones y cada átomo tiene dos electrones en su capa de valencia.



El enlace covalente se estudiará con más detalle en el Capítulo 2.

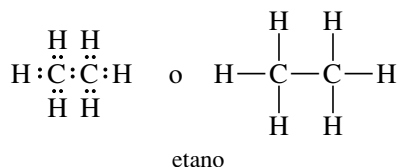
Una forma de simbolizar el enlace en una molécula covalente consiste en usar **estructuras de Lewis**. En una estructura de Lewis cada electrón de valencia se simboliza por un punto. Un par de electrones de enlace se simboliza por un par de puntos o por una línea (—). Se ha de intentar que todos los átomos tengan sus propias configuraciones de gas noble: dos electrones en el caso del hidrógeno y octetos para los elementos de la segunda fila de la tabla periódica.

Considere, por ejemplo, la estructura de Lewis del metano ( $\text{CH}_4$ ):



El carbono contribuye con cuatro electrones de valencia y cada hidrógeno aporta uno, dando un total de ocho electrones. Todos estos ocho electrones rodean al carbono dando lugar a un octeto y cada átomo de hidrógeno comparte dos de los electrones.

La estructura de Lewis para el etano ( $\text{C}_2\text{H}_6$ ) es más compleja:



Una vez más, se han colocado los electrones de valencia (14) y se han distribuido de forma que cada átomo de carbono quede rodeado por ocho electrones y cada hidrógeno por dos. La única estructura posible para el etano es la que se ha mostrado anteriormente, con los dos átomos de carbono compartiendo un par de electrones y cada átomo de hidrógeno compartiendo dos con uno de los carbonos. La estructura del etano muestra las características más importantes del carbono (su habilidad para formar enlaces fuertes carbono-carbono).

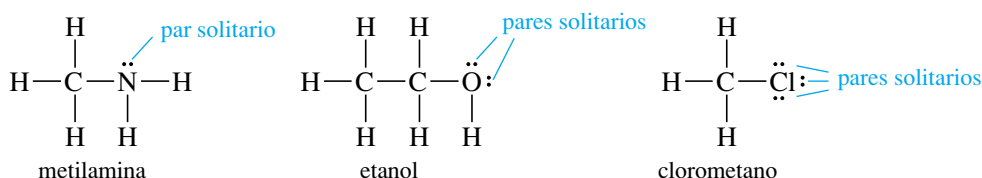
Los electrones de la capa de valencia que *no* son compartidos entre dos átomos reciben el nombre de **electrones no enlazantes**. Un par de electrones no enlazantes a menudo también es conocido como un **par solitario**. Los átomos de oxígeno, de nitrógeno y los halógenos (F, Cl, Br, I) normalmente tienen electrones no enlazantes en sus compuestos

## 1.4 Estructuras de Lewis

## SUGERENCIA PARA RESOLVER PROBLEMAS

Las estructuras de Lewis son la forma de representar los enlaces en química orgánica. Aprender a representarlas de forma rápida y correctamente será muy útil a lo largo de este curso.

estables. Estos pares solitarios de electrones no enlazantes ayudan a determinar la reactividad de sus compuestos. Las estructuras de Lewis siguientes muestran un par solitario de electrones en el átomo de nitrógeno de la metilamina y dos pares solitarios en el átomo de oxígeno del etanol. Los átomos de los halógenos normalmente tienen tres pares solitarios, como se muestra en la estructura del clorometano.



Una estructura de Lewis correcta debería mostrar los pares solitarios de electrones. Los químicos orgánicos a menudo dibujan estructuras de Lewis omitiendo la mayoría o todos los pares solitarios de electrones. Éstas no son estructuras correctas de Lewis porque uno se ha de imaginar el número de electrones no enlazantes.

### PROBLEMA 1.2

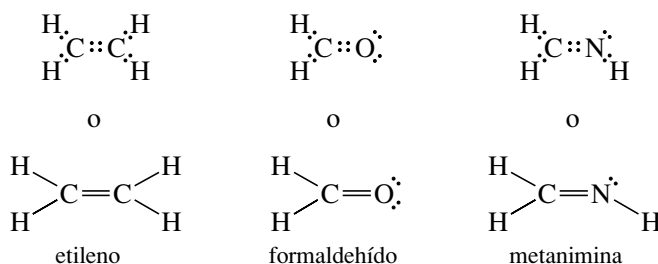
Dibuje las estructuras de Lewis de los siguientes compuestos:

- |  |  |
|--|--|
| (a) amoníaco, $\text{NH}_3$                        | (b) agua, $\text{H}_2\text{O}$                               |
| (c) ión hidronio, $\text{H}_3\text{O}^+$           | (d) propano, $\text{C}_3\text{H}_8$                          |
| (e) etilamina, $\text{CH}_3\text{CH}_2\text{NH}_2$ | (f) dimetil éter, $\text{CH}_3\text{OCH}_3$                  |
| (g) fluoroetano, $\text{CH}_3\text{CH}_2\text{F}$  | (h) 2-propanol, $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$ |
| (i) borano, $\text{BH}_3$                          | (j) trifluoruro de boro, $\text{BF}_3$                       |

Explique qué es inusual en el enlace de los compuestos (i) y (j).

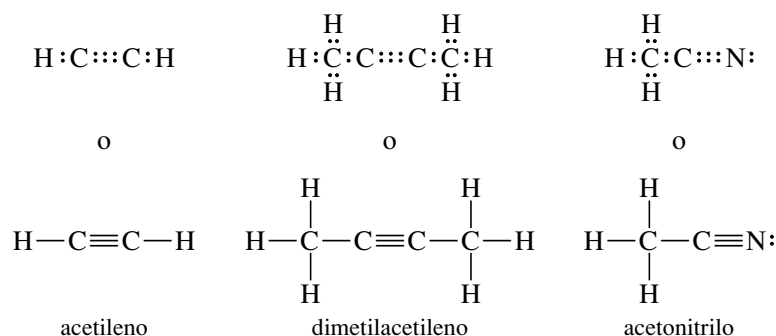
## 1.5 Enlace múltiple

Al representar las estructuras de Lewis en la Sección 1.4, se pusieron un par de electrones entre cada dos átomos. La compartición de un par de electrones entre dos átomos se conoce como **enlace sencillo**. Muchas moléculas comparten con sus átomos adyacentes dos o incluso tres pares de electrones; cuando se comparten dos pares se da el nombre de **enlace doble** y cuando se comparten tres pares se da el nombre de **enlace triple**. El etileno ( $\text{C}_2\text{H}_4$ ) es un compuesto orgánico con un doble enlace. Cuando se representan las estructuras de Lewis para el etileno, la única forma de conseguir que los dos átomos de carbono tengan octetos es mediante la compartición de dos pares de electrones. El ejemplo siguiente muestra compuestos orgánicos con dobles enlaces. En cada caso, se comparten cuatro electrones (dos pares) entre dos átomos para formar octetos. Una doble línea ( $=$ ) simboliza el doble enlace.



El acetileno, cuando se combina con el oxígeno, arde con una llama intensa que tiene diversas aplicaciones. Se puede utilizar para soldar las piezas de un puente bajo el agua o para reparar las tuberías de un oleoducto en Siberia.

El acetileno ( $\text{C}_2\text{H}_2$ ) tiene un triple enlace. Su estructura de Lewis muestra los tres pares de electrones entre los dos átomos de carbono para que formen un octeto. Una línea triple ( $\equiv$ ) simboliza el triple enlace.



Todas estas estructuras de Lewis muestran que el carbono normalmente forma cuatro enlaces en compuestos orgánicos neutros. El nitrógeno generalmente forma tres enlaces y el oxígeno dos. El hidrógeno y los halógenos normalmente forman un enlace. El número de enlaces que normalmente puede formar un átomo se conoce como **valencia**. El carbono es tetravalente, el nitrógeno trivalente, el oxígeno divalente, y el hidrógeno y los halógenos monovalentes. Si se recuerda el número usual de enlaces de estos elementos, se podrán escribir estructuras orgánicas con mucha facilidad. Si una estructura se representa de forma que cada átomo tenga el número de enlaces que le corresponden, la estructura de Lewis será correcta.

### RESUMEN Modelos de enlace más frecuentes (sin carga)

	$\begin{array}{c}   \\ -\text{C}- \\   \end{array}$	$\begin{array}{c} \cdot\cdot \\ -\text{N}- \\   \end{array}$	$\begin{array}{c} \cdot\cdot \\ -\text{O}- \\ \cdot\cdot \end{array}$	$-\text{H}$	$\begin{array}{c} \cdot\cdot \\ -\text{Cl}: \end{array}$
	carbono	nitrógeno	oxígeno	hidrógeno	halógenos
valencia:	4	3	2	1	1
pares solitarios:	0	1	2	0	3

### SUGERENCIA PARA RESOLVER PROBLEMAS

Estos «números de enlaces usuales» pueden ser sencillos o estar combinados en dobles y triples enlaces. Por ejemplo, los tres enlaces del nitrógeno podrían corresponder a tres enlaces sencillos, a un enlace sencillo y uno doble, o a un triple enlace ( $:\text{N}\equiv\text{N}:$ ). En los problemas hay que considerar todas las posibilidades.

### PROBLEMA 1.3

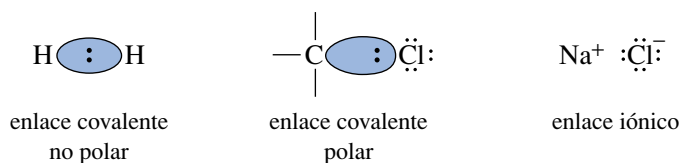
Escriba la estructura de Lewis para cada una de las siguientes fórmulas moleculares:

- |   |   |                            |
|---|---|----------------------------|
| (a) $\text{N}_2$                                | (b) $\text{HCN}$                              | (c) $\text{HONO}$          |
| (d) $\text{CO}_2$                               | (e) $\text{H}_2\text{CNH}$                    | (f) $\text{HCO}_2\text{H}$ |
| (g) $\text{C}_2\text{H}_3\text{Cl}$             | (h) $\text{HNNH}$                             | (i) $\text{C}_3\text{H}_6$ |
| (j) $\text{C}_3\text{H}_4$ (dos dobles enlaces) | (k) $\text{C}_3\text{H}_4$ (un triple enlace) |                            |

### PROBLEMA 1.4

Rodee con un círculo los pares solitarios (pares de electrones no enlazantes) en las estructuras representadas en el Problema 1.3.

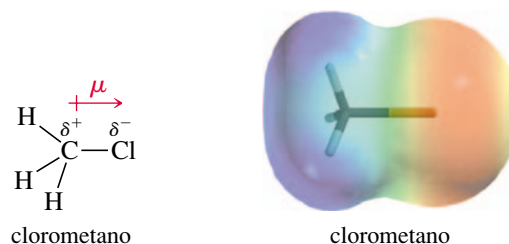
Un enlace cuyos electrones están igualmente compartidos por los dos átomos recibe el nombre de **enlace covalente no polar**. El enlace en la molécula de  $\text{H}_2$  y el enlace  $\text{C}-\text{C}$  en el etano son enlaces covalentes no polares. En la mayoría de enlaces entre dos elementos diferentes los electrones del enlace están atraídos de forma diferente por cada uno de los dos núcleos. Cuando la compartición del par de electrones del enlace no es igual para los dos átomos, a este enlace se le conoce como **enlace covalente polar**.



## 1.6 La electronegatividad y la polaridad de enlace

► **Figura 1.6**

El clorometano contiene un enlace polar carbono-cloro con una carga negativa parcial en el cloro y una carga positiva parcial en el carbono. El mapa de potencial electrostático muestra una región roja (rica en electrones) alrededor de la carga negativa parcial y una región azul (pobre en electrones) alrededor de la carga positiva parcial. El resto de colores indican valores intermedios de potencial electrostático.



Cuando el carbono se enlaza al cloro, por ejemplo, los electrones de enlace son atraídos más fuertemente hacia el átomo de cloro, por lo que el átomo de carbono adquirirá una pequeña carga positiva parcial y el átomo de cloro esa misma cantidad de carga pero de signo negativo. La Figura 1.6 muestra el enlace polar carbono-cloro del clorometano. Nosotros simbolizaremos la polaridad de enlace por una flecha que tenga como origen la carga positiva del enlace polar, y sobre este origen un signo positivo. La polaridad de un enlace se mide por su **momento dipolar** ( $\mu$ ), definido por el producto de la carga (separación de las cargas  $\delta^+$  y  $\delta^-$ ) y la longitud del enlace. El símbolo  $\delta^+$  significa «una pequeña cantidad de carga positiva» y el símbolo  $\delta^-$  «una pequeña cantidad de carga negativa».

La Figura 1.6 también muestra un **mapa de potencial electrostático (MPE)** para el clorometano, que usa colores para representar la distribución de la carga calculada en una molécula. El rojo indica regiones ricas en electrones y el azul regiones pobres en electrones. El naranja, amarillo y verde indican niveles intermedios de potencial electrostático. En el clorometano, la región roja muestra la carga negativa parcial del cloro y la región azul indica la carga positiva parcial de los átomos de carbono y de hidrógeno.

A menudo se usan las **electronegatividades** como guía para predecir si un determinado enlace será polar y la dirección del momento dipolar. La escala de electronegatividad de Pauling, la que comúnmente utilizan los químicos orgánicos, se basa en las propiedades del enlace y es muy útil para predecir la polaridad de los enlaces covalentes. Los elementos con electronegatividades más altas atraen con más fuerza a los electrones de enlace. No obstante, en un enlace entre dos átomos diferentes, el átomo con la electronegatividad más alta es el extremo negativo del dipolo. La Figura 1.7 muestra las electronegatividades de Pauling para algunos de los elementos importantes de los compuestos orgánicos.

Obsérvese que la electronegatividad aumenta de izquierda a derecha a lo largo de la tabla periódica. El nitrógeno, el oxígeno y los halógenos son más electronegativos que el carbono; el sodio, el litio y el magnesio son menos electronegativos. La electronegatividad del hidrógeno es parecida a la del carbono, por lo que el enlace C—H normalmente se considera no polar. La polaridad de los enlaces y de las moléculas se tratará con más detalle en la Sección 2.9.

**PROBLEMA 1.5**

Haga uso de las electronegatividades para predecir los momentos dipolares de los siguientes enlaces:

- (a) C—Cl      (b) C—O      (c) C—N      (d) C—S      (e) C—B  
(f) N—Cl      (g) N—O      (h) N—S      (i) N—B      (j) B—Cl

► **Figura 1.7**

Electronegatividades de algunos de los elementos que se encuentran en los compuestos orgánicos.

H 2.2							
Li 1.0	Be 1.6	B 1.8	C 2.5	N 3.0	O 3.4	F 4.0	
Na 0.9	Mg 1.3	Al 1.6	Si 1.9	P 2.2	S 2.6	Cl 3.2	
K 0.8						Br 3.0	
						I 2.7	

En los enlaces polares, las cargas parciales ( $\delta^+$  y  $\delta^-$ ) de los átomos del enlace son *reales*. Las **cargas formales** proporcionan un método de seguimiento de los electrones, pero pueden corresponder o no a cargas reales. En la mayoría de los casos, si la estructura de Lewis muestra que un átomo tiene una carga formal, quiere decir que tiene parte de esa carga. El concepto de carga formal ayuda a determinar qué átomos tienen mayor cantidad de carga en una molécula y ver que hay átomos cargados en moléculas que son neutras globalmente.

Para calcular las cargas formales, hay que contar cuántos electrones contribuyen a la carga de cada átomo y comparar ese número con el número de electrones de valencia que hay en el átomo neutro y aislado (dado por el número de grupo en la tabla periódica). Los electrones que contribuyen a la carga de un átomo son:

1. *Todos* sus electrones no compartidos (no enlazantes).
2. *La mitad* de los electrones (enlazantes) que comparte con otros átomos, o un electrón de cada par de enlace.

La carga formal de un átomo determinado puede ser calculada mediante la fórmula:

$$\text{carga formal (CF)} = [\text{número de grupo}] - [\text{electrones no enlazantes}] - \frac{1}{2} [\text{electrones compartidos}]$$

### PROBLEMA RESUELTO 1.1

Calcule la carga formal (CF) de cada átomo de las estructuras siguientes:

(a) Metano ( $\text{CH}_4$ )

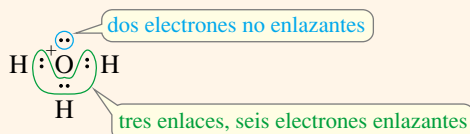


### SOLUCIÓN

Cada átomo de hidrógeno del metano tiene un par enlazante de electrones (dos electrones compartidos). La mitad de los dos electrones compartidos es un electrón de valencia y es lo que el hidrógeno necesita para ser neutro. Los átomos de hidrógeno con un enlace son neutros formalmente:  $\text{CF} = 1 - 0 - 1 = 0$ .

El átomo de carbono tiene cuatro pares de electrones enlazantes (ocho electrones). La mitad de los ocho electrones compartidos, esto es, cuatro electrones son los que el carbono (grupo IVA) necesita para ser neutro. El carbono es formalmente neutro cuando tiene cuatro enlaces:  $\text{CF} = 4 - 0 - \frac{1}{2}(8) = 0$ .

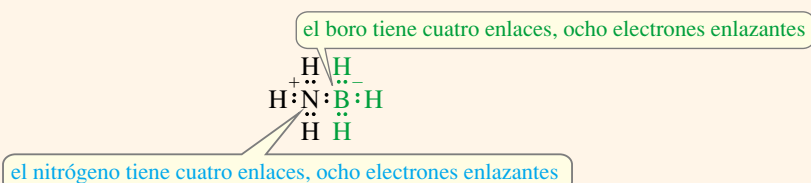
(b) Ión hidronio,  $\text{H}_3\text{O}^+$



### SOLUCIÓN

Cuando se representa la estructura de Lewis para este ión, se utilizan ocho electrones: seis del oxígeno y tres de los hidrógenos, menos uno porque el ión tiene una carga positiva. Cada hidrógeno tiene un enlace y es formalmente neutro. El oxígeno está rodeado por un octeto, con seis electrones enlazantes y dos electrones no enlazantes. La mitad de los electrones enlazantes más todos los electrones no enlazantes contribuyen a la carga:  $6/2 + 2 = 5$ ; pero el oxígeno (grupo VIA) necesita seis electrones de valencia para ser neutro, por este motivo, el átomo de oxígeno tiene una carga formal de  $+1$ :  $\text{CF} = 6 - 2 - \frac{1}{2}(6) = +1$ .

(c)  $\text{H}_3\text{N} - \text{BH}_3$



## 1.7 Cargas formales

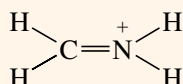
**SOLUCIÓN**

Éste es un compuesto neutro donde los átomos individuales están cargados formalmente. La estructura de Lewis muestra que tanto el nitrógeno como el boro tienen cuatro pares de electrones enlazantes. Los dos átomos, boro y nitrógeno, tienen  $8/2 = 4$  electrones que contribuyen a sus cargas. El nitrógeno (grupo V) necesita cinco electrones de valencia para ser neutro, por lo que su carga formal es  $+1$ . El boro (grupo III) sólo necesita tres electrones de valencia para ser neutro, por lo que su carga formal es  $-1$ .

$$\text{Nitrógeno: } CF = 5 - 0 - \frac{1}{2}(8) = +1$$

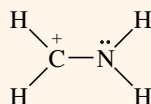
$$\text{Boro: } CF = 3 - 0 - \frac{1}{2}(8) = -1$$

(d)  $[\text{H}_2\text{CNH}_2]^+$

**SOLUCIÓN**

En esta estructura, tanto el carbono como el nitrógeno tienen cuatro pares de electrones enlazantes. Con cuatro enlaces, el carbono es formalmente neutro; no obstante, el nitrógeno es del grupo V, por lo que su carga positiva formal es:  $CF = 5 - 0 - 4 = +1$ .

Este compuesto también podría ser representado con la siguiente estructura de Lewis:



En esta estructura, el átomo de carbono tiene tres enlaces con seis electrones enlazantes que, si se dividen entre dos,  $6/2 = 3$ , se observa que el carbono tiene un electrón menos de los cuatro que necesita para ser neutro formalmente:  $CF = 4 - 0 - \frac{1}{2}(6) = +1$ .

El nitrógeno tiene seis electrones enlazantes y dos electrones no enlazantes. Si se hace el cálculo  $6/2 + 2 = 5$ , se observa que el nitrógeno es neutro en esta segunda estructura:

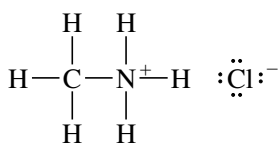
$$CF = 5 - 2 - \frac{1}{2}(6) = 0$$

El significado de estas dos estructuras de Lewis se discute en la Sección 1.9.

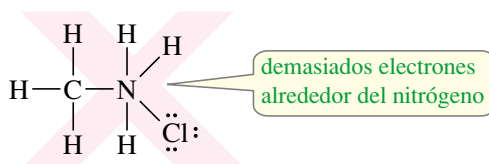
La mayoría de los compuestos orgánicos sólo contienen un número pequeño de elementos bastante comunes, normalmente con el octeto de electrones completo. La tabla resumen de la página siguiente indica la naturaleza de los enlaces más habituales, utilizando líneas para representar los pares de electrones enlazantes. Utilice estas reglas de cálculo de las cargas formales para comprobar las cargas que se dan en las estructuras. Si las estructuras se entienden bien, será fácil representar los compuestos orgánicos y sus iones de forma rápida y correcta.

## 1.8 Estructuras iónicas

Algunos compuestos orgánicos contienen enlaces iónicos. Por ejemplo, la estructura del cloruro de metilamonio ( $\text{CH}_3\text{NH}_3\text{Cl}$ ) no se puede representar si solamente se utilizan enlaces covalentes; esto requeriría que el nitrógeno tuviese cinco enlaces, lo que implicaría diez electrones en la capa de valencia. La estructura correcta contiene un ión cloruro enlazado iónicamente al resto de la estructura.



cloruro de metilamonio



no se puede representar mediante enlaces covalentes

## RESUMEN

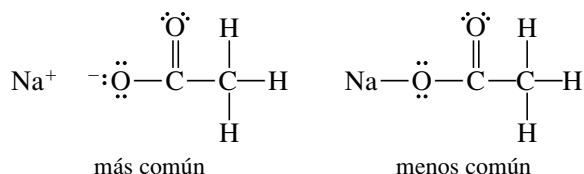
## Modelos de enlace más frecuentes en los compuestos e iones orgánicos

Átomo	Electrones de valencia	Cargado positivamente	Neutro	Cargado negativamente
B	3		(no octeto) $\begin{array}{c} \text{—B—} \\   \end{array}$	$\begin{array}{c}   \\ \text{—B—} \\   \end{array}$
C	4	$\begin{array}{c} + \\ \text{—C—} \\   \end{array}$ (no octeto)	$\begin{array}{c}   \\ \text{—C—} \\   \end{array}$	$\begin{array}{c} \cdot\cdot \\ \text{—C—} \\   \end{array}$
N	5	$\begin{array}{c}   \\ \text{—N}^+ \\   \end{array}$	$\begin{array}{c} \cdot\cdot \\ \text{—N—} \\   \end{array}$	$\begin{array}{c} \cdot\cdot \\ \text{—N—} \\   \end{array}$
O	6	$\begin{array}{c} \cdot\cdot \\ \text{—O}^+ \\   \end{array}$	$\begin{array}{c} \cdot\cdot \\ \text{—O—} \\   \end{array}$	$\begin{array}{c} \cdot\cdot \\ \text{—O—} \\   \end{array}$
halógeno	7	$\begin{array}{c} \cdot\cdot \\ \text{—Cl}^+ \\   \end{array}$	$\begin{array}{c} \cdot\cdot \\ \text{—Cl:} \end{array}$	$\begin{array}{c} \cdot\cdot \\ \text{:Cl:}^- \end{array}$

SUGERENCIA  
PARA RESOLVER PROBLEMAS

Esta tabla es muy importante. Haz un número de problemas suficientes como para familiarizarte con estos modelos de enlace, tal que puedas saber cuándo otros modelos son incorrectos o bien inusuales.

Algunas moléculas se pueden representar tanto en forma covalente como iónica. Por ejemplo, el acetato de sodio ( $\text{NaOCOCH}_3$ ) se puede representar tanto con un enlace covalente como con un enlace iónico entre el sodio y el oxígeno. Como el sodio normalmente forma enlaces iónicos con el oxígeno ( $\text{NaOH}$ ), la estructura con enlace iónico es la que se prefiere. En general, los enlaces entre átomos con gran diferencia de electronegatividad (2 o más) normalmente se representan como compuestos iónicos.



## PROBLEMA 1.6

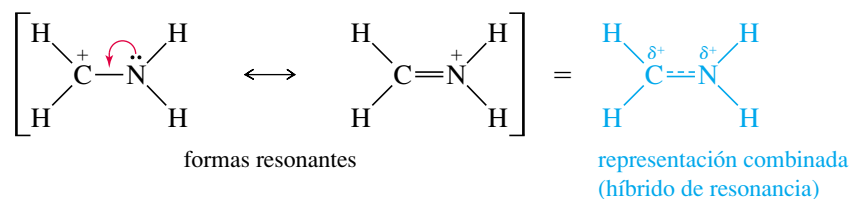
Dibuje las estructuras de Lewis de los siguientes compuestos e iones, diciendo cuál es su carga formal apropiada:

- |   |                                 |
|---|---------------------------------|
| (a) $[\text{CH}_3\text{OH}_2]^+$          | (b) $\text{NH}_4\text{Cl}$      |
| (c) $(\text{CH}_3)_2\text{NH}_2\text{Cl}$ | (d) $\text{NaOCH}_3$            |
| (e) $^+\text{CH}_3$                       | (f) $^-\text{CH}_3$             |
| (g) $\text{NaBH}_4$                       | (h) $\text{NaBH}_3\text{CN}$    |
| (i) $(\text{CH}_3)_2\text{O—BF}_3$        | (j) $[\text{HONH}_3]^+$         |
| (k) $\text{KOC}(\text{CH}_3)_3$           | (l) $[\text{H}_2\text{C=OH}]^+$ |

## 1.9A Híbridos de resonancia

Algunas de las estructuras de los compuestos no es adecuado representarlas mediante una sola estructura de Lewis. Cuando son posibles dos o más estructuras de enlace de valencia, que difieren sólo en la colocación de los electrones, la molécula suele mostrar características de las dos estructuras. A estas estructuras diferentes se las conoce como **estructuras de resonancia** o **formas resonantes**, ya que no son compuestos diferentes, sino formas diferentes de representar el mismo compuesto. La molécula real se dice que corresponde a un **híbrido de resonancia** de sus formas resonantes. En el Problema resuelto 1.1(d) se mostró cómo el ión  $[\text{H}_2\text{CNH}_2]^+$  se podía representar por cualquiera de las siguientes formas de resonancia:

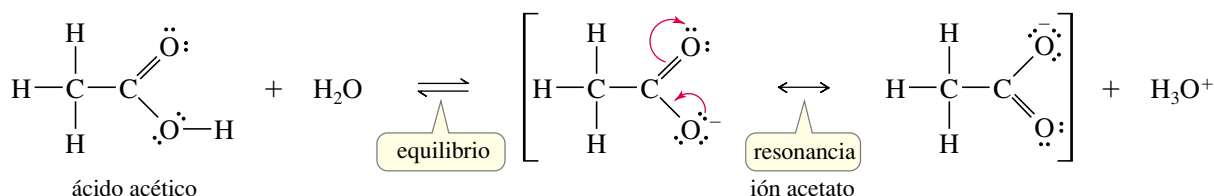
1.9  
Resonancia



La estructura real de este ión es un híbrido de resonancia de las dos estructuras. En la molécula real, la carga positiva está **deslocalizada** (extendida) entre el átomo de carbono y el de nitrógeno. En la forma resonante de la izquierda, la carga positiva está en el carbono, pero el carbono no tiene un octeto. Los electrones no enlazantes del nitrógeno se pueden mover por el enlace (tal como indica la flecha roja) dando una segunda estructura con un doble enlace entre el nitrógeno que tiene carga positiva y el carbono que posee un octeto. La representación combinada de las dos formas de resonancia en una sola representación da lugar a una carga compartida entre el nitrógeno y el carbono.

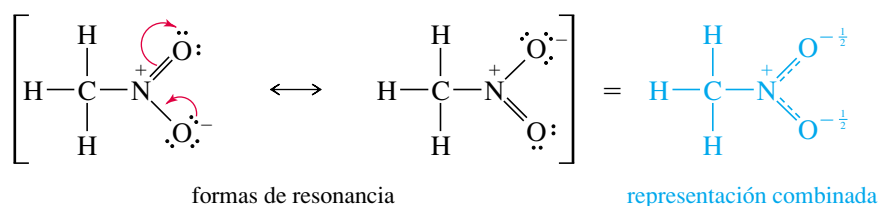
El extender la carga positiva sobre dos átomos hace que el ión sea más estable que en el caso de que la carga positiva estuviera localizada solamente sobre el carbono o sobre el nitrógeno. Se dice que este catión está **estabilizado por resonancia**. La resonancia es más importante cuando permite que una carga esté deslocalizada entre dos o más átomos, como en el ejemplo mencionado.

La estabilización por resonancia desempeña un papel crucial en la química orgánica, especialmente en la química de compuestos que tienen dobles enlaces. Se usará frecuentemente el concepto de resonancia a lo largo de este curso. Por ejemplo, la acidez del ácido acético (véase abajo) se incrementa por efecto de la resonancia. Cuando el ácido acético pierde un protón, el ión acetato resultante tiene una carga negativa deslocalizada sobre los dos átomos de oxígeno. Cada átomo de oxígeno posee la mitad de la carga negativa y su deslocalización estabiliza el ión. Cada uno de los enlaces carbono-oxígeno es intermedio entre un enlace doble y un enlace sencillo, por lo que se dice que su *orden de enlace* es de  $1\frac{1}{2}$ .



Se usará una sola flecha con doble punta entre las formas de resonancia (a menudo puestas entre corchetes) para indicar que la estructura real es un híbrido de las estructuras de Lewis representadas. Por otra parte, un equilibrio se representará por dos flechas con sentidos opuestos.

Algunas moléculas sin carga también tienen estructuras de resonancia estabilizadas con la misma carga formal positiva y negativa. Se pueden representar dos estructuras de Lewis para el nitrometano ( $\text{CH}_3\text{NO}_2$ ), pero las dos estructuras tienen una carga positiva formal en el nitrógeno y una carga negativa en uno de los oxígenos. Por tanto, el nitrometano tiene una carga positiva en el átomo de nitrógeno y una carga negativa extendida por igual sobre los dos átomos de oxígeno. Los enlaces N—O están entre un enlace sencillo y uno doble, tal como se indica en la representación combinada siguiente:



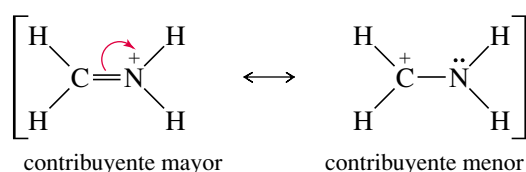
Recuerde que las formas de resonancia individuales no existen como especies químicas independientes. La molécula no «resuena» entre esas estructuras, es un híbrido con



características de ambas estructuras. Una analogía sería una mula, que es un híbrido de un caballo y un burro. La mula no «resuena» entre parecerse a un caballo o a un burro; simplemente es una mula, con el amplio dorso de un caballo y las grandes orejas de un burro.

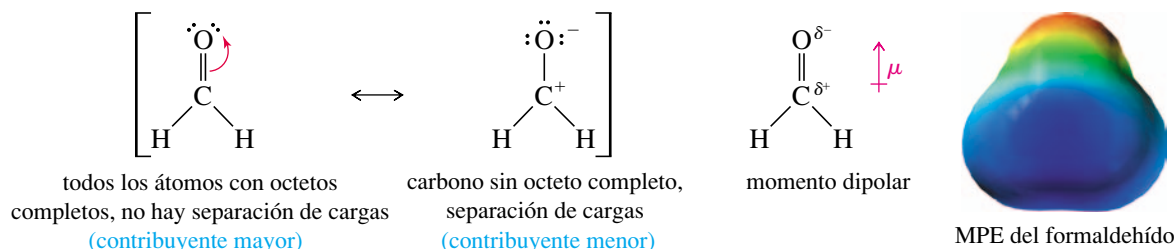
### 1.9B Contribución mayor o menor de las formas resonantes al híbrido de resonancia

Dos o más estructuras de Lewis correctas para un mismo compuesto pueden o no representar distribuciones de electrones de igual energía. A pesar de que formas de resonancia separadas no existen, se pueden estimar sus energías relativas como si existieran. La mayoría de las formas de resonancia estables son representaciones más cercanas de la molécula real que las menos estables. Las dos formas de resonancia del apartado anterior, para el ión acetato, tienen enlaces similares e idéntica energía. Lo mismo se puede decir para las dos formas de resonancia del nitrometano. Las formas de resonancia siguientes, por el contrario, tienen enlaces diferentes.



Las estructuras anteriores no tienen la misma energía estimada. La primera estructura tiene la carga positiva en el nitrógeno. La segunda tiene la carga positiva en el carbono, y el átomo de carbono no posee un octeto completo. La primera estructura es más estable ya que tiene un enlace adicional y todos los átomos tienen octetos completos. Muchos iones estables tienen una carga positiva en el átomo de nitrógeno con cuatro enlaces (*véase* la tabla resumen de la página 13). A la forma de resonancia más estable se la conoce como la **contribuyente mayor** y a la forma menos estable como la **contribuyente menor**. La estructura del compuesto real se parece más al contribuyente mayor que al contribuyente menor.

Muchas moléculas orgánicas tienen contribuyentes de resonancia mayor y menor. El formaldehído ( $\text{H}_2\text{C}=\text{O}$ ) se puede representar con una carga negativa en el oxígeno, equilibrada por una carga positiva en el carbono. Esta forma de resonancia polar tiene mayor energía estimada que la estructura con doble enlace, porque tiene separación de cargas, menos enlaces y un átomo de carbono cargado positivamente con un octeto incompleto. La estructura con cargas separadas es solamente un contribuyente menor, pero ayuda a explicar por qué el enlace  $\text{C}=\text{O}$  del formaldehído es muy polar, con una carga positiva parcial en el carbono y una carga negativa parcial en el oxígeno. El mapa de potencial electrostático (MPE) también muestra una región rica en electrones (rojo) alrededor del oxígeno y una región pobre en electrones (azul) alrededor del carbono en el formaldehído.



Cuando se representan las formas de resonancia, se intenta dibujar estructuras que sean lo más bajas posible en energía. Las mejores candidatas son las que tienen un número máximo de octetos y el máximo número de enlaces. Además, las estructuras tienen que tener la mínima cantidad de separación de cargas.

*Sólo los electrones pueden estar deslocalizados.* Al contrario que los electrones, los núcleos no pueden estar deslocalizados, deben permanecer en el mismo lugar, con las mismas distancias de enlace y los mismos ángulos en todos los contribuyentes a la resonancia. Las reglas generales siguientes serán útiles para representar estructuras de resonancias.

## SUGERENCIA PARA RESOLVER PROBLEMAS

Para comparar las formas de resonancia se pueden utilizar los siguientes criterios, comenzando por el más importante:

1. Tantos octetos como sea posible.
2. Tantos enlaces como sea posible.
3. Si hay carga negativa se coloca en los átomos electronegativos.
4. La menor separación de cargas posible.

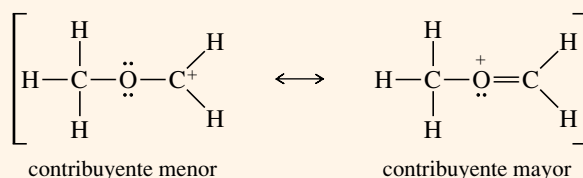
1. Todas las estructuras de resonancia deben ser estructuras de Lewis válidas para el compuesto.
2. Sólo se puede cambiar la posición de los electrones de una estructura a otra (los electrones de los dobles enlaces y pares solitarios son los que se cambian con más frecuencia). El núcleo no se puede cambiar de posición y los ángulos de enlace han de ser los mismos.
3. El número de electrones desapareados (si hay alguno) debe permanecer igual. La mayoría de los compuestos estables no tienen electrones desapareados y todos los electrones deben permanecer apareados en todas las estructuras de resonancia.
4. El contribuyente mayor a la resonancia es el que tiene menor energía.  
Los buenos contribuyentes generalmente tienen todos los octetos satisfechos, con el máximo número de enlaces covalentes que sea posible y con una separación de cargas lo menor posible. Las cargas negativas son más estables en los átomos más electronegativos.
5. La estabilización por resonancia es más importante cuando sirve para deslocalizar una carga entre dos o más átomos.

### PROBLEMA RESUELTO 1.2

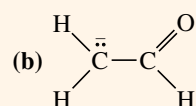
Para cada uno de los siguientes compuestos, represente las formas de resonancia importantes. Indique qué estructuras tienen contribuyentes mayores y menores, o si tienen la misma energía.

(a)  $[\text{CH}_3\text{OCH}_2]^+$

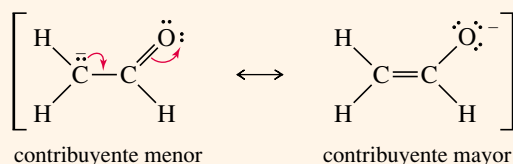
#### SOLUCIÓN



La primera estructura (menor) tiene un átomo de carbono con sólo seis electrones a su alrededor. La segunda estructura (mayor) tiene octetos en todos los átomos y un enlace adicional.



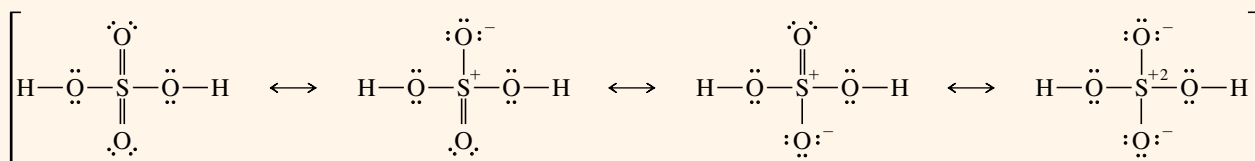
#### SOLUCIÓN



Las dos estructuras tienen octetos en el átomo de oxígeno y en el de carbono, y tienen el mismo número de enlaces. La primera estructura tiene la carga negativa en el carbono y la segunda la tiene en el oxígeno. El oxígeno es más electronegativo que el carbono, por lo tanto, la segunda estructura es el contribuyente mayor.

(c)  $\text{H}_2\text{SO}_4$

#### SOLUCIÓN



La primera estructura, con más enlaces y menor separación de carga, es posible porque el azufre es un elemento de la tercera fila de la tabla periódica con orbitales *d* accesibles, lo que le da la posibilidad de expandir aparentemente su octeto. Por ejemplo, el  $\text{SF}_6$  es un compuesto estable con 12 electrones alrededor del azufre. Sin embargo, algunos cálculos teóricos sugieren que la última estructura representada, con octetos en todos los átomos, podría ser la contribuyente mayor a la resonancia. No se puede predecir siempre el contribuyente mayor de un híbrido de resonancia.

**PROBLEMA 1.7**

Represente las formas de resonancia importantes de las siguientes moléculas e iones:

- (a)  $\text{CO}_3^{2-}$  (b)  $\text{NO}_3^-$  (c)  $\text{NO}_2^-$  (d)  $\text{H}_2\text{C}=\text{CH}-\text{CH}_2^+$   
 (e)  $\text{H}_2\text{C}=\text{CH}-\text{CH}_2^-$  (f)  $\text{SO}_4^{2-}$  (g)  $[\text{CH}_3\text{C}(\text{OCH}_3)_2]^+$

**PROBLEMA 1.8**

Para cada uno de los siguientes compuestos, represente las formas de resonancia importantes. Indique qué estructuras son las contribuyentes mayores y menores a la resonancia, o si tienen la misma energía.

- (a)  $[\text{H}_2\text{CNO}_2]^-$  (b)  $\text{H}_2\text{C}=\text{CH}-\text{NO}_2$  (c)  $[\text{H}_2\text{COH}]^+$   
 (d)  $\text{H}_2\text{CNN}$  (e)  $[\text{H}_2\text{CCN}]^-$  (f)  $\text{H}_2\text{N}-\overset{+}{\text{CH}}-\text{CH}=\text{CH}-\text{NH}_2$   
 (g)  $\text{H}-\overset{\text{O}}{\parallel}{\text{C}}-\overset{-}{\text{CH}}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$  (h)  $\text{H}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}_2$

**SUGERENCIA****PARA RESOLVER PROBLEMAS**

Quando se representan formas de resonancia para iones, observe cómo se puede deslocalizar la carga entre varios átomos. Intente colocar una carga negativa sobre elementos electronegativos como el oxígeno y el nitrógeno. Intente, así mismo, colocar una carga positiva sobre todos los carbonos que sea posible, pero especialmente sobre los átomos que puedan alojar la carga positiva y tener un octeto completo; por ejemplo, el oxígeno (con tres enlaces) o el nitrógeno (con cuatro enlaces).

Los químicos orgánicos utilizan varias clases de fórmulas para representar los compuestos orgánicos. Algunas de estas fórmulas incluyen una notación específica que requiere una explicación. Las **fórmulas estructurales** indican qué átomos están enlazados a otros. Hay dos tipos de fórmulas estructurales: las estructuras de Lewis completas y las fórmulas estructurales condensadas. Además, hay varias formas de representar fórmulas estructurales condensadas. Según se ha visto, una estructura de Lewis simboliza un par de electrones enlazantes como un par de puntos o como una línea (—). Los pares solitarios de electrones se muestran como pares de puntos.

**1.10****Fórmulas estructurales****1.10A Fórmulas estructurales condensadas**

Las **fórmulas estructurales condensadas** (Tabla 1.2) se representan sin mostrar todos los enlaces individuales. En una estructura condensada, cada átomo central se representa junto a los átomos a los que está enlazado. Los átomos enlazados a un átomo central a menudo se escriben a continuación del átomo central ( $\text{CH}_3\text{CH}_3$  en lugar de  $\text{H}_3\text{C}-\text{CH}_3$ ) incluso aunque no sea el orden del verdadero enlace. En muchos casos, si hay dos o más grupos idénticos, se puede utilizar un paréntesis y un subíndice para representar a todos estos grupos. Los electrones no enlazantes raramente se representan en las fórmulas estructurales condensadas.

**TABLA 1.2** Ejemplos de fórmulas estructurales condensadas

Compuesto	Estructura de Lewis	Fórmula estructural condensada
etano	$\begin{array}{c} \text{H} & \text{H} \\   &   \\ \text{H}-\text{C} & -\text{C}-\text{H} \\   &   \\ \text{H} & \text{H} \end{array}$	$\text{CH}_3\text{CH}_3$
isobutano	$\begin{array}{c} \text{H} & \text{H} & \text{H} \\   &   &   \\ \text{H}-\text{C} & -\text{C}- & \text{C}-\text{H} \\   & &   \\ \text{H} & & \text{H} \\ &   & \\ & \text{H}-\text{C}-\text{H} \\ &   & \\ & \text{H} & \end{array}$	$(\text{CH}_3)_3\text{CH}$
n-hexano	$\begin{array}{c} \text{H} & \text{H} & \text{H} & \text{H} & \text{H} & \text{H} \\   &   &   &   &   &   \\ \text{H}-\text{C} & -\text{C} & -\text{C} & -\text{C} & -\text{C} & -\text{C}-\text{H} \\   &   &   &   &   &   \\ \text{H} & \text{H} & \text{H} & \text{H} & \text{H} & \text{H} \end{array}$	$\text{CH}_3(\text{CH}_2)_4\text{CH}_3$

(continúa en la página siguiente)

**TABLA 1.2** (continuación)

Compuesto	Estructura de Lewis	Fórmula estructural condensada
dietil éter	$  \begin{array}{ccccccc}  & \text{H} & \text{H} & & \text{H} & \text{H} & \\  &   &   & &   &   & \\  \text{H} & - \text{C} & - \text{C} & - \ddot{\text{O}} & - \text{C} & - \text{C} & - \text{H} \\  &   &   & &   &   & \\  & \text{H} & \text{H} & & \text{H} & \text{H} &   \end{array}  $	$\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$ o $\text{CH}_3\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_3$ o $(\text{CH}_3\text{CH}_2)_2\text{O}$
etanol	$  \begin{array}{ccccccc}  & \text{H} & \text{H} & & & & \\  &   &   & & & & \\  \text{H} & - \text{C} & - \text{C} & - \ddot{\text{O}} & - \text{H} \\  &   &   & & & & \\  & \text{H} & \text{H} & & & &   \end{array}  $	$\text{CH}_3\text{CH}_2\text{OH}$
alcohol isopropílico	$  \begin{array}{ccccccc}  & \text{H} & & \ddot{\text{O}} & - \text{H} & \text{H} & \\  &   & &   & &   & \\  \text{H} & - \text{C} & - \text{C} & - & \text{C} & - \text{H} \\  &   &   & &   & & \\  & \text{H} & \text{H} & & \text{H} & &   \end{array}  $	$(\text{CH}_3)_2\text{CHOH}$
dimetilamina	$  \begin{array}{ccccccc}  & \text{H} & & & \text{H} & & \\  &   & & &   & & \\  \text{H} & - \text{C} & - \ddot{\text{N}} & - & \text{C} & - \text{H} \\  &   & & &   & & \\  & \text{H} & & & \text{H} & &   \end{array}  $	$(\text{CH}_3)_2\text{NH}$

Cuando se escribe una fórmula estructural condensada para un compuesto que contiene enlaces dobles o triples, los enlaces múltiples con frecuencia se representan igual que en las estructuras de Lewis. La Tabla 1.3 muestra ejemplos de fórmulas estructurales condensadas que contienen enlaces múltiples. Observe que el grupo  $-\text{CHO}$  de un aldehído y el grupo  $-\text{COOH}$  de un ácido carboxílico se enlazan de forma diferente a como sugiere la notación condensada.

Como se puede observar en las Tablas 1.2 y 1.3, la diferencia entre una fórmula estructural de Lewis completa y una fórmula estructural condensada puede ser confusa. Los químicos con frecuencia representan las fórmulas con algunas partes condensadas y otras

**TABLA 1.3** Fórmulas estructurales condensadas para dobles y triples enlaces

Compuesto	Estructura de Lewis	Fórmula estructural condensada
2-buteno	$  \begin{array}{ccccccc}  & \text{H} & \text{H} & & \text{H} & & \\  &   &   & &   & & \\  \text{H} & - \text{C} & - \text{C} = \text{C} & - \text{C} & - \text{H} \\  &   & &   &   & & \\  & \text{H} & & \text{H} & \text{H} & &   \end{array}  $	$\text{CH}_3\text{CHCHCH}_3$ o $\text{CH}_3\text{CH}=\text{CHCH}_3$
acetonitrilo	$  \begin{array}{ccccccc}  & \text{H} & & & & & \\  &   & & & & & \\  \text{H} & - \text{C} & - \text{C} \equiv \text{N} & : \\  &   & & & & & \\  & \text{H} & & & & &   \end{array}  $	$\text{CH}_3\text{CN}$ o $\text{CH}_3\text{C}\equiv\text{N}$
acetaldehído	$  \begin{array}{ccccccc}  & \text{H} & & \ddot{\text{O}} & & & \\  &   & &    & & & \\  \text{H} & - \text{C} & - & \text{C} & - \text{H} \\  &   & & & & & \\  & \text{H} & & & & &   \end{array}  $	$\text{CH}_3\text{CHO}$ o $\text{CH}_3\overset{\text{O}}{\underset{  }{\text{C}}}\text{H}$
acetona	$  \begin{array}{ccccccc}  & \text{H} & & \ddot{\text{O}} & & \text{H} & \\  &   & &    & &   & \\  \text{H} & - \text{C} & - & \text{C} & - & \text{C} & - \text{H} \\  &   & & & &   & \\  & \text{H} & & & & \text{H} &   \end{array}  $	$\text{CH}_3\text{COCH}_3$ o $\text{CH}_3\overset{\text{O}}{\underset{  }{\text{C}}}\text{CH}_3$
ácido acético	$  \begin{array}{ccccccc}  & \text{H} & & \ddot{\text{O}} & & & \\  &   & &    & & & \\  \text{H} & - \text{C} & - & \text{C} & - \ddot{\text{O}} & - \text{H} \\  &   & & & & & \\  & \text{H} & & & & &   \end{array}  $	$\text{CH}_3\text{COOH}$ o $\text{CH}_3\overset{\text{O}}{\underset{  }{\text{C}}}-\text{OH}$ o $\text{CH}_3\text{CO}_2\text{H}$

completamente desarrolladas. El estudiante debería trabajar con las diferentes formas de representar las fórmulas para entender su significado.

### PROBLEMA 1.9

Represente las estructuras de Lewis completas para las siguientes fórmulas estructurales condensadas:

- (a)  $\text{CH}_3(\text{CH}_2)_3\text{CH}(\text{CH}_3)_2$  (b)  $(\text{CH}_3)_2\text{CHCH}_2\text{Cl}$  (c)  $\text{CH}_3\text{CH}_2\text{COCHCH}_2$   
 (d)  $\text{CH}_3\text{CH}_2\text{CHO}$  (e)  $\text{CH}_3\text{COCN}$  (f)  $(\text{CH}_3)_3\text{CCOOH}$  (g)  $(\text{CH}_3\text{CH}_2)_2\text{CO}$

### 1.10B Fórmulas lineoangulares

Otra forma de representar las estructuras orgánicas es la **fórmula lineoangular**, algunas veces llamada **estructura esquelética** o de barras. Las fórmulas lineoangulares con frecuencia se usan en los compuestos cíclicos y muy ocasionalmente en los lineales. En una fórmula lineoangular, los enlaces están representados por líneas y los átomos de carbono vienen dados por los vértices o puntos de encuentro de dos líneas, o el punto del principio o final de la línea en el caso de los extremos. Los átomos de nitrógeno, de oxígeno y los halógenos se escriben con su símbolo, pero los átomos de hidrógeno frecuentemente no se simbolizan a no ser que vayan unidos a elementos que se han simbolizado. Se supone que cada átomo de carbono tiene los suficientes átomos de hidrógeno para que el total de sus enlaces sea cuatro. Los electrones no enlazantes raramente se representan. La Tabla 1.4 muestra algunos ejemplos de estas representaciones lineoangulares.

**TABLA 1.4** Ejemplos de representaciones lineoangulares

Compuesto	Estructura condensada	Fórmula lineoangular
hexano	$\text{CH}_3(\text{CH}_2)_4\text{CH}_3$	
2-hexeno	$\text{CH}_3\text{CH}=\text{CHCH}_2\text{CH}_2\text{CH}_3$	
3-hexanol	$\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{CH}_2\text{CH}_3$	
2-ciclohexenona		
2-metilciclohexanol		
ácido nicotínico (vitamina, también llamada niacina)		

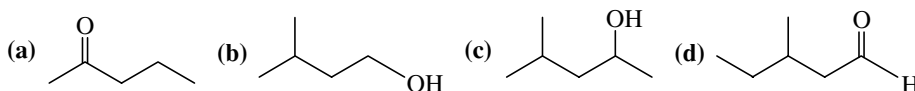
### PROBLEMA 1.10

Escriba la estructura de Lewis correspondiente a las siguientes estructuras lineoangulares:

- (a)
- (b)
- (c)
- (d)
- (e)
- (f)
- (g)
- (h)

**PROBLEMA 1.11**

Represente las fórmulas estructurales condensadas correspondientes a las siguientes estructuras lineoangulares:



## 1.11

### Fórmulas moleculares y fórmulas empíricas

Antes de poder escribir las posibles fórmulas estructurales de un compuesto, se necesita saber su fórmula molecular. La **fórmula molecular** simplemente informa del número de átomos de cada elemento que hay en una molécula de un compuesto. Por ejemplo, la fórmula molecular del 1-butanol es  $C_4H_{10}O$ .



1-butanol, fórmula molecular  $C_4H_{10}O$

**Cálculo de la fórmula empírica** Las fórmulas moleculares se pueden determinar mediante un proceso que consta de dos pasos. El primer paso es la determinación de la **fórmula empírica**, o relación relativa entre los elementos presentes en la molécula. Suponga, por ejemplo, que en un compuesto desconocido, por análisis elemental cuantitativo, se encontró que contenía un 40.00% de carbono y un 6.67% de hidrógeno. La masa restante, 53.33%, se supone que era oxígeno. Para pasar esos números a una fórmula empírica, se puede seguir un procedimiento simple:

1. Suponga que la muestra contiene 100 g, por lo que los valores porcentuales dan el número de gramos de cada elemento. Dividiendo el número de gramos de cada elemento por la masa atómica se obtiene el número de moles de ese átomo en los 100 g de muestra.
2. Divida cada uno de los números de moles obtenidos en el paso anterior por el número más pequeño y redondee a la cifra entera más próxima. Este paso ha de conducir a la relación existente, expresada en números enteros, entre los elementos de la molécula.

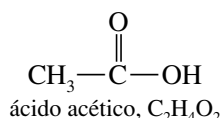
Para el compuesto desconocido, con los datos anteriores y siguiendo los pasos indicados, se obtendrían los siguientes resultados:

$$\begin{aligned} \frac{40.0 \text{ g C}}{12.0 \text{ g/mol}} &= 3.33 \text{ mol C}; & \frac{3.33 \text{ mol}}{3.33 \text{ mol}} &= 1 \\ \frac{6.67 \text{ g H}}{1.01 \text{ g/mol}} &= 6.60 \text{ mol H}; & \frac{6.60 \text{ mol}}{3.33 \text{ mol}} &= 1.98 \approx 2 \\ \frac{53.3 \text{ g O}}{16.0 \text{ g/mol}} &= 3.33 \text{ mol O}; & \frac{3.33 \text{ mol}}{3.33 \text{ mol}} &= 1 \end{aligned}$$

En el primer cálculo se divide el número de gramos de carbono por 12, el número de gramos de hidrógeno por 1 y el número de gramos de oxígeno por 16. Se comparan los resultados dividiendo todos los valores obtenidos por el número más pequeño, 3.33. El resultado final da una relación de un átomo de carbono por dos de hidrógeno y uno de oxígeno. Este resultado nos dice que la fórmula empírica es  $C_1H_2O_1$  o  $CH_2O$ , que muestra solamente la relación de los elementos. La fórmula molecular puede ser un múltiplo cualquiera de la fórmula empírica, porque cualquier múltiplo también tiene la misma relación numérica entre los átomos de sus elementos. Fórmulas moleculares posibles son  $CH_2O$ ,  $C_2H_4O_2$ ,  $C_3H_6O_3$ ,  $C_4H_8O_4$ , etc.

**Cálculo de la fórmula molecular** ¿Cómo se sabe cuál es la fórmula molecular correcta? Se puede elegir el verdadero múltiplo de la fórmula empírica cuando se conoce la masa molecular. Las masas moleculares de una sustancia se pueden determinar por métodos como el *descenso crioscópico* o el *aumento ebulloscópico* de un disolvente cuando contiene la sustancia desconocida a una concentración molar. Si el compuesto es volátil, se puede convertir en gas y utilizar su volumen para determinar el número de moles por la *ley de los gases ideales*. En la actualidad existen métodos entre los que se incluye la *espectrometría de masas*, que será tratada en el Capítulo 11.

Para el ejemplo anterior (fórmula empírica:  $\text{CH}_2\text{O}$ ) supondremos que la masa molecular es aproximadamente 60. La masa de una unidad de  $\text{CH}_2\text{O}$  es 30, por lo que el compuesto contendrá el doble número de átomos. La fórmula molecular será  $\text{C}_2\text{H}_4\text{O}_2$ . Este compuesto podría ser el ácido acético.



En los Capítulos 12, 13 y 15 se usarán técnicas espectroscópicas para determinar la estructura completa de un compuesto una vez que se conozca su fórmula molecular.

### PROBLEMA 1.12

Escriba la fórmula empírica y la fórmula molecular a partir de los análisis elementales siguientes. En cada caso, proponga al menos una estructura que corresponda a la fórmula molecular.

	C	H	N	Cl	PM(*)
(a)	40.0%	6.67%	0	0	90
(b)	32.0%	6.67%	18.7%	0	75
(c)	37.2%	7.75%	0	55.0%	64
(d)	38.4%	4.80%	0	56.8%	125

(\*) Peso molecular.

### SUGERENCIA

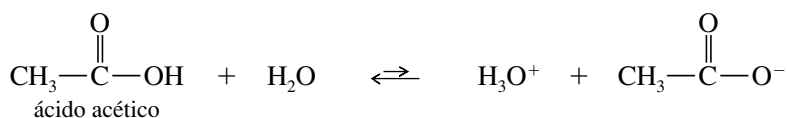
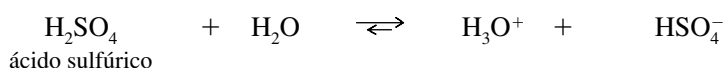
#### PARA RESOLVER PROBLEMAS

Si un análisis elemental no suma el 100%, el porcentaje que falta se supone que es de oxígeno.

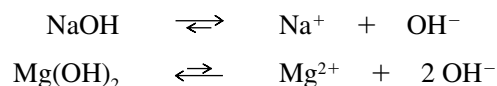
Las propiedades y la reactividad de los ácidos y de las bases son fundamentales para el estudio de la química orgánica. Hay que saber exactamente qué quieren decir los términos **ácido** y **base**. La mayoría de la gente estaría de acuerdo en que el  $\text{H}_2\text{SO}_4$  es un ácido y el  $\text{NaOH}$  una base. ¿El  $\text{BF}_3$  es un ácido o es una base? ¿El etileno ( $\text{H}_2\text{C}=\text{CH}_2$ ) es un ácido o una base? Para responder a estas preguntas se necesitan entender las tres definiciones diferentes de los ácidos y de las bases: la definición de Arrhenius, la de Brønsted-Lowry y la de Lewis.

La primera clasificación de los compuestos ácidos se hizo basándose en su sabor agrio. Los términos latinos *acidus* (agrio) y *acetum* (vinagre) dieron lugar a los términos actuales de *ácido* y *ácido acético*. Los compuestos alcalinos (bases) eran sustancias que neutralizaban a los ácidos, tales como la caliza y las cenizas de las plantas (en árabe, *al kalai*).

La *teoría de Arrhenius* se desarrolló al final del siglo diecinueve y definía los ácidos como sustancias que se disocian en el agua para formar iones  $\text{H}_3\text{O}^+$ . Se asumió que los ácidos más fuertes, tales como el ácido sulfúrico ( $\text{H}_2\text{SO}_4$ ), se disociaban mucho más que los ácidos débiles, tales como el ácido acético ( $\text{CH}_3\text{COOH}$ ).



Según la definición de Arrhenius, las bases son sustancias que se disocian en solución acuosa para formar iones hidroxilo. Por otra parte se consideró que las bases fuertes, tales como el  $\text{NaOH}$ , se disociaban más que las débiles o que aquellas que se disuelven moderadamente, como el  $\text{Mg}(\text{OH})_2$ .



La acidez o basicidad de una solución acuosa (agua) de una sustancia se mide por la concentración de  $\text{H}_3\text{O}^+$  en dicha disolución. Este valor también permite conocer implícitamente la concentración de  $\text{OH}^-$ , ya que estas dos concentraciones están relacionadas entre sí por la constante de ionización del agua:

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.00 \times 10^{-14} \quad (\text{a } 24^\circ\text{C})$$

## 1.12

### Ácidos y bases de Arrhenius

En las soluciones neutras la concentración de  $[\text{H}_3\text{O}^+]$  y de  $[\text{OH}^-]$  son iguales,

$$[\text{H}_3\text{O}^+] = [\text{OH}^-] = 1.0 \times 10^{-7} \text{ M} \text{ en una solución neutra}$$

Las soluciones ácidas y básicas poseen un exceso de  $[\text{H}_3\text{O}^+]$  o de  $[\text{OH}^-]$ , respectivamente.

$$\text{ácidas: } [\text{H}_3\text{O}^+] > 10^{-7} \text{ M} \text{ y } [\text{OH}^-] < 10^{-7} \text{ M}$$

$$\text{básicas: } [\text{H}_3\text{O}^+] < 10^{-7} \text{ M} \text{ y } [\text{OH}^-] > 10^{-7} \text{ M}$$

Como estas concentraciones pueden abarcar un amplio rango de valores, la acidez o basicidad de una solución normalmente se mide en escala logarítmica. El **pH** se define como el logaritmo (en base 10), cambiado de signo, de la concentración de  $\text{H}_3\text{O}^+$ .

$$\text{pH} = -\log_{10}[\text{H}_3\text{O}^+]$$

Una solución neutra tiene un pH de 7, una solución ácida tiene un pH menor que 7 y una solución básica tiene un pH mayor que 7.

### PROBLEMA 1.13

Calcule el pH de las siguientes soluciones:

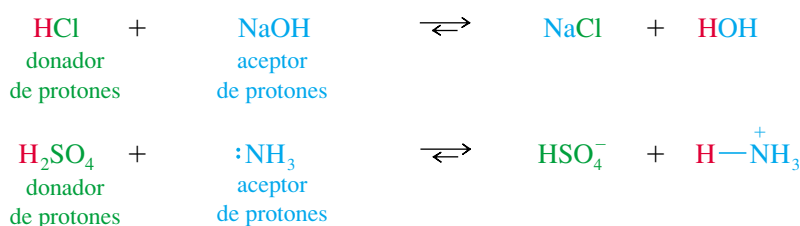
- (a) 5.00 g de HBr en 100 mL de solución acuosa.
- (b) 1.50 g de NaOH en 50 mL de solución acuosa.

La definición de Arrhenius fue una contribución importante para poder entender muchos ácidos y muchas bases, pero no explica por qué un compuesto como el amoníaco ( $\text{NH}_3$ ) neutraliza los ácidos, a pesar de no tener un ión hidróxido en su fórmula molecular. En la Sección 1.13 se explica una teoría más versátil de ácidos y bases que incluye al amoníaco y a una variedad más amplia de ácidos y bases orgánicos.

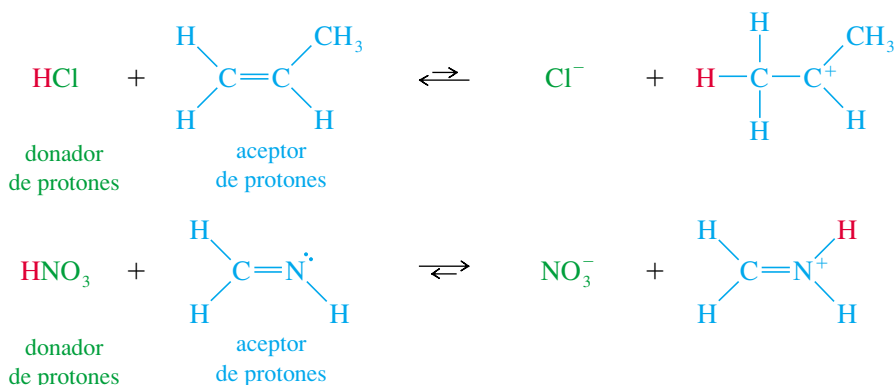
## 1.13 Ácidos y bases de Brønsted-Lowry

En 1923, Brønsted y Lowry definieron los ácidos y las bases teniendo en cuenta su capacidad de liberar o captar protones, respectivamente. Un **ácido de Brønsted-Lowry** es cualquier especie que puede donar un protón, y una **base de Brønsted-Lowry** es cualquier especie que puede aceptar un protón. Estas definiciones también incluyen todos los ácidos y bases de Arrhenius, ya que los compuestos que se disocian para dar  $\text{H}_3\text{O}^+$  son donadores de protones y los compuestos que se disocian para dar  $\text{OH}^-$  son aceptores de protones (el ión hidróxido acepta un protón para formar  $\text{H}_2\text{O}$ ).

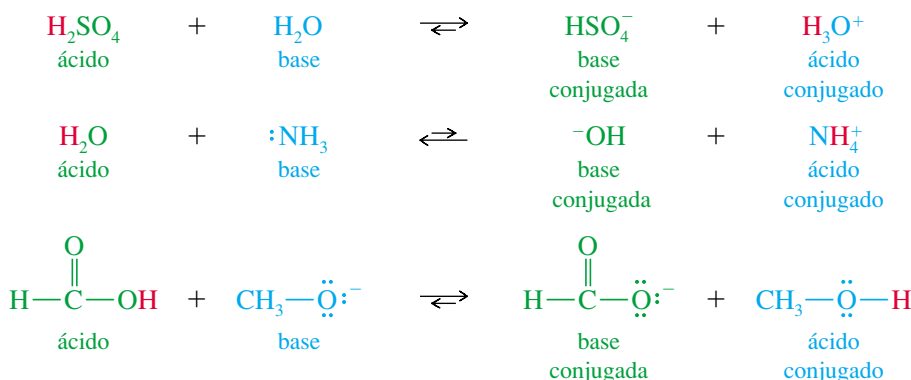
Además de los ácidos y bases de Arrhenius, la definición de Brønsted-Lowry incluye también las bases que no tienen iones hidróxido, y que pueden aceptar protones. Observe los ejemplos siguientes de ácidos capaces de ceder protones a las bases. El NaOH es una base tanto si se considera la definición de Arrhenius o la de Brønsted-Lowry. Los tres ejemplos siguientes son bases de Brønsted-Lowry pero no bases de Arrhenius, ya que no tienen iones hidróxido.





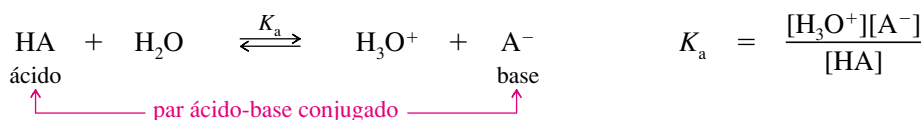


Cuando una base acepta un protón, se convierte en un ácido capaz de devolver ese protón. Cuando un ácido cede un protón, se convierte en una base capaz de aceptar de nuevo ese protón. Uno de los principios más importantes de la definición de Brønsted-Lowry es el concepto de **ácidos y bases conjugados**. Por ejemplo, el  $\text{NH}_3$  y el  $\text{NH}_4^+$  forman un par de ácido y base conjugados; el  $\text{NH}_3$  es la base, cuando acepta un protón, se transforma en el ácido conjugado,  $\text{NH}_4^+$ . Muchos compuestos (por ejemplo, el agua) pueden reaccionar como un ácido o como una base. A continuación se dan algunos ejemplos de pares ácido-base conjugados:



### 1.13A Fuerza de los ácidos

La fuerza de un ácido de Brønsted-Lowry se expresa de forma similar a la definición de Arrhenius, teniendo en cuenta su grado de ionización en agua. La reacción general de un ácido (HA) con agua es la siguiente:



A la  $K_a$  se la conoce con el nombre de *constante de disociación del ácido* y su valor indica la fuerza relativa del ácido. Cuanto más fuerte es el ácido, más se disocia, dando un valor de  $K_a$  mayor. Las constantes de disociación de un ácido varían en un intervalo amplio. Los ácidos fuertes se ionizan casi completamente en agua y sus constantes de disociación son superiores a 1. La mayoría de los ácidos orgánicos son ácidos débiles, con valores de  $K_a$  menores que  $10^{-4}$ . Muchos compuestos orgánicos son ácidos extremadamente débiles; por ejemplo, el metano y el etano tienen un carácter ácido muy débil, su  $K_a$  es inferior a  $10^{-40}$ .

Debido a este amplio margen de valores, las constantes de disociación ácida frecuentemente se expresan en escala logarítmica. El  $\text{p}K_a$  de un ácido se define de forma parecida al pH: logaritmo (en base 10), con signo negativo, de la  $K_a$ .

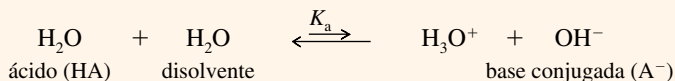
$$\text{p}K_a = -\log_{10} K_a$$

**PROBLEMA RESUELTO 1.3**

Calcule la  $K_a$  y el  $pK_a$  del agua.

**SOLUCIÓN**

El equilibrio que define la  $K_a$  del agua es:



El agua se comporta en esta disolución como ácido y como disolvente. La expresión del equilibrio es:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]}$$

Donde  $[\text{H}_3\text{O}^+][\text{OH}^-] = 1.00 \times 10^{-14}$ , constante del producto de ionización del agua.

La concentración de moléculas de  $\text{H}_2\text{O}$  en el agua simplemente es el número de moles de agua en 1 L (aproximadamente 1 kg).

$$\frac{1000 \text{ g/L}}{18 \text{ g/mol}} = 55.6 \text{ mol/L}$$

Haciendo la sustitución:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]} = \frac{1.00 \times 10^{-14}}{55.6} = 1.8 \times 10^{-16} \text{ M}$$

El logaritmo de  $1.8 \times 10^{-16}$  es  $-15.7$ , por lo que el  $pK_a$  del agua es 15.7.

**SUGERENCIA  
PARA RESOLVER PROBLEMAS**

En la mayor parte de los casos, el  $pK_a$  de un ácido coincide con el valor del pH de un ácido disociado en un 50%. A un pH menor (más ácido), el ácido estará menos disociado; a un pH mayor (más básico), el ácido estará más disociado.

Los ácidos fuertes generalmente tienen valores de  $pK_a$  próximos a 0 y los ácidos débiles, como la mayoría de los ácidos orgánicos, tienen valores superiores a 4. *Los ácidos más débiles tienen valores de  $pK_a$  más elevados.* La Tabla 1.5 recoge los valores de  $K_a$  y  $pK_a$  de algunos de los compuestos inorgánicos y orgánicos más habituales. Observa que los valores de  $pK_a$  aumentan cuando los valores de  $K_a$  disminuyen.

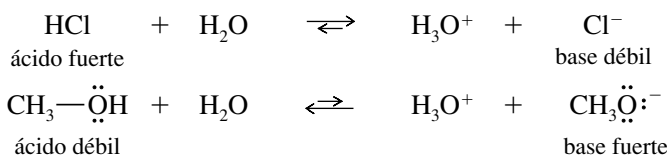
**PROBLEMA 1.14**

El amoníaco se encuentra en la Tabla 1.5 de dos formas, la forma básica y su ácido conjugado.

- Explique cómo el amoníaco puede actuar como base y como ácido. ¿Cuál de estas dos formas es más habitual en las soluciones acuosas?
- Explique por qué el agua puede actuar como ácido y como base.
- Explique por qué el metanol ( $\text{CH}_3\text{OH}$ ) puede comportarse como ácido y como base. Escriba una ecuación para la reacción del metanol con el ácido sulfúrico.

**1.13B Fuerza de las bases**

La fuerza de un ácido es inversa a la fuerza de su base conjugada. Si un ácido (HA) es fuerte, su base conjugada ( $\text{A}^-$ ) será débil, al ser estable en su forma aniónica; de lo contrario, el ácido HA no perdería fácilmente sus protones. Por lo tanto, la base conjugada de un ácido fuerte será una base débil. Por otra parte, si un ácido es débil, su conjugado es una base fuerte.

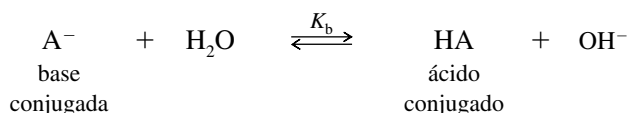


En la reacción de un ácido con una base, el equilibrio generalmente está desplazado hacia la formación de los ácidos y bases *débiles*. Por ejemplo, en las reacciones anteriores, el  $\text{H}_3\text{O}^+$  es un ácido más débil que el HCl, pero un ácido más fuerte que el  $\text{CH}_3\text{OH}$ ; esto conlleva que el  $\text{H}_2\text{O}$  sea una base más fuerte que el  $\text{Cl}^-$ , pero más débil que el  $\text{CH}_3\text{O}^-$ .

**TABLA 1.5** Fuerza relativa de algunos ácidos inorgánicos y orgánicos frecuentes, y sus bases conjugadas

	Ácido		Base conjugada	$K_a$	$pK_a$
ácidos fuertes	<b>HCl</b> ácido clorhídrico	$+ H_2O \rightleftharpoons H_3O^+ + Cl^-$	ion cloruro	$1.6 \times 10^2$	-2.2
	<b>HF</b> ácido fluorhídrico	$+ H_2O \rightleftharpoons H_3O^+ + F^-$	ion fluoruro	$6.8 \times 10^{-4}$	3.17
	$\begin{array}{c} O \\    \\ H-C-OH \end{array}$ ácido fórmico	$+ H_2O \rightleftharpoons H_3O^+ + \begin{array}{c} O \\    \\ H-C-O^- \end{array}$	ion formiato	$1.7 \times 10^{-4}$	3.76
	$\begin{array}{c} O \\    \\ CH_3-C-OH \end{array}$ ácido acético	$+ H_2O \rightleftharpoons H_3O^+ + \begin{array}{c} O \\    \\ CH_3-C-O^- \end{array}$	acetano ion	$1.8 \times 10^{-5}$	4.74
ácidos débiles	<b><math>H-C \equiv N:</math></b> ácido cianhídrico	$+ H_2O \rightleftharpoons H_3O^+ + :C \equiv N:$	ion cianuro	$6.0 \times 10^{-10}$	9.22
	<b><math>^+NH_4</math></b> ion amonio	$+ H_2O \rightleftharpoons H_3O^+ + :NH_3$	amoniaco	$5.8 \times 10^{-10}$	9.24
	<b><math>CH_3-OH</math></b> alcohol metílico	$+ H_2O \rightleftharpoons H_3O^+ + CH_3O^-$	metóxido ion	$3.2 \times 10^{-16}$	15.5
	<b><math>H_2O</math></b> agua	$+ H_2O \rightleftharpoons H_3O^+ + HO^-$	ion hidróxido	$1.8 \times 10^{-16}$	15.7
muy débil	<b><math>NH_3</math></b> amoniaco	$+ H_2O \rightleftharpoons H_3O^+ + :\ddot{N}H_2$	ion amiduro	$10^{-33}$	33
no ácido	<b><math>CH_4</math></b> metano	$+ H_2O \rightleftharpoons H_3O^+ + :\ddot{C}H_3$	anión metilo	$<10^{-40}$	$>40$

La fuerza de una base se mide de forma similar a la de los ácidos, usando la constante de equilibrio de la reacción de hidrólisis:



La constante de equilibrio ( $K_b$ ) para esta reacción se conoce con el nombre de *constante de disociación de la base* para la base  $A^-$ . Debido a que esta constante tiene un amplio rango de valores, frecuentemente se expresa en forma logarítmica. El  $pK_b$  se define como el logaritmo (en base 10), cambiado de signo, de la  $K_b$ .

$$K_b = \frac{[HA][OH^-]}{[A^-]} \quad pK_b = -\log_{10} K_b$$

Cuando se multiplica  $K_a$  por  $K_b$ , se puede apreciar cómo la acidez de un ácido está relacionada con la basicidad de su base conjugada:

Las propiedades ácido-base de muchos productos naturales son importantes de cara a su aislamiento, a su distribución en el cuerpo y a justificar sus efectos terapéuticos. Por ejemplo, la morfina (p. 2), que se aísla de las adormideras (opio), llega al cerebro como base libre, en la que el nitrógeno no está cargado. Sin embargo, son sus especies cargadas las que actúan como analgésicas.

$$(K_a)(K_b) = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]} = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$$

constante del producto de ionización del agua

$$(K_a)(K_b) = 10^{-14}$$

Aplicando logaritmos:

$$\text{p}K_a + \text{p}K_b = -\log 10^{-14} = 14$$

El producto de  $K_a$  por  $K_b$  siempre es igual a la constante del producto iónico del agua,  $10^{-14}$ . Si el valor de  $K_a$  es grande, el valor de  $K_b$  será pequeño; es decir, cuanto más fuerte es un ácido, más débil es su base conjugada. De forma similar, un valor pequeño de  $K_a$  (ácido débil) implica un valor grande de  $K_b$  (base fuerte).

Cuanto más fuerte es un ácido, más débil es su base conjugada.

Cuanto más débil es un ácido, más fuerte es su base conjugada.

Las reacciones ácido-base favorecen la formación de ácidos más débiles y/o bases más débiles.

## SUGERENCIA PARA RESOLVER PROBLEMAS

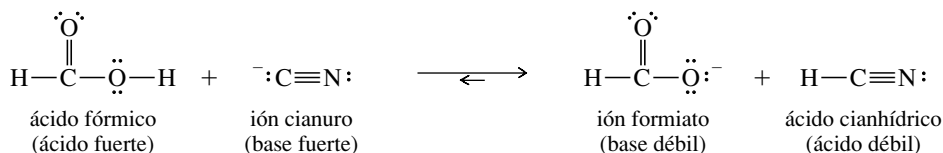
Un ácido donará un protón a la base conjugada de cualquier ácido que sea más débil (menor  $K_a$  o mayor  $\text{p}K_a$ ).

### PROBLEMA 1.15 (parcialmente resuelto)

Escriba las ecuaciones para las siguientes reacciones ácido-base. Utilice la información de la Tabla 1.5 para predecir si el equilibrio favorecerá a los reactivos o a los productos.

- |  |  |
|--|--|
| (a) $\text{HCOOH} + ^-\text{CN}$           | (b) $\text{CH}_3\text{COO}^- + \text{CH}_3\text{OH}$ |
| (c) $\text{CH}_3\text{OH} + \text{NaNH}_2$ | (d) $\text{NaOCH}_3 + \text{HCN}$                    |
| (e) $\text{HCl} + \text{H}_2\text{O}$      | (f) $\text{H}_3\text{O}^+ + \text{CH}_3\text{O}^-$   |

**Solución para (a):** el ión cianuro es la base conjugada del HCN; puede aceptar un protón del ácido fórmico:



Observando la Tabla 1.5, se aprecia que el ácido fórmico ( $\text{p}K_a = 3.76$ ) es un ácido más fuerte que el HCN ( $\text{p}K_a = 9.22$ ) y que el cianuro es una base más fuerte que el formiato. Resultan favorecidos, pues, los productos ácido y base más débiles.

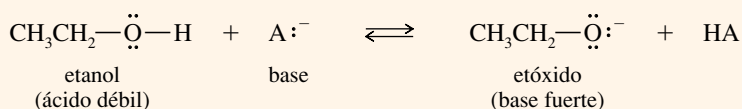
### PROBLEMA RESUELTO 1.4

Cada uno de los compuestos siguientes puede actuar como un ácido. Escriba la reacción de cada compuesto con una base general ( $\text{A}^-$ ) y la estructura de Lewis de la base conjugada que se obtiene.

- |                                       |                              |                              |
|---------------------------------------|------------------------------|------------------------------|
| (a) $\text{CH}_3\text{CH}_2\text{OH}$ | (b) $\text{CH}_3\text{NH}_2$ | (c) $\text{CH}_3\text{COOH}$ |
|---------------------------------------|------------------------------|------------------------------|

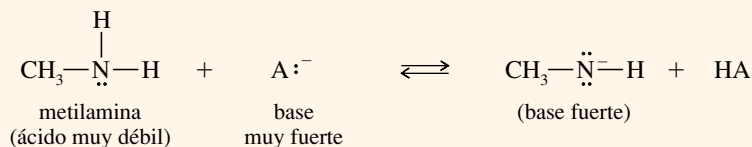
#### SOLUCIÓN

- (a) El etanol ( $\text{CH}_3\text{CH}_2\text{OH}$ ) puede perder el protón del grupo  $\text{O}-\text{H}$  para formar una base conjugada que es un ión orgánico análogo al ión hidroxilo.

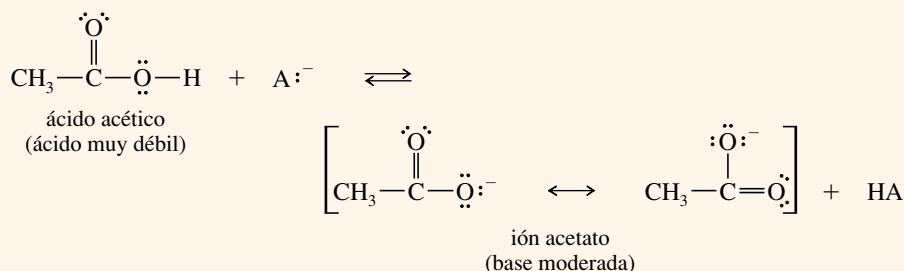


(Los protones del grupo  $\text{C}-\text{H}$  son mucho menos ácidos que los protones del grupo  $\text{O}-\text{H}$ , porque el carbono es menos electronegativo que el oxígeno y, por lo tanto, la carga negativa es menos estable en el carbono.)

- (b) La metilamina ( $\text{CH}_3\text{NH}_2$ ) es un ácido muy débil. Una base muy fuerte le puede sustraer un protón y dar lugar a una base conjugada fuerte.



- (c) El ácido acético ( $\text{CH}_3\text{COOH}$ ) es un ácido moderadamente fuerte. Su base conjugada es el ión acetato que está estabilizado por resonancia.

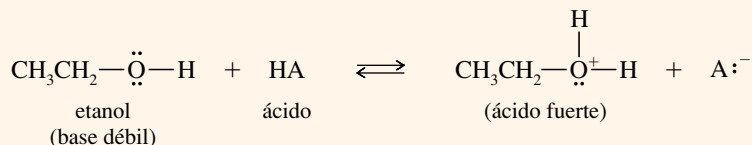


### PROBLEMA RESUELTO 1.5

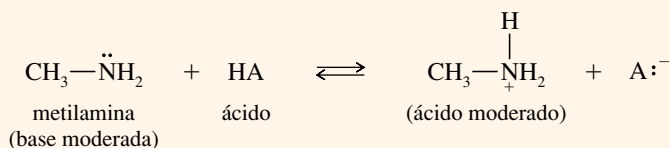
Cada uno de los compuestos del Problema resuelto 1.4 también pueden reaccionar como una base. Escriba la reacción de cada compuesto con un ácido general (HA) y las estructuras de Lewis del ácido conjugado que se obtiene.

### SOLUCIÓN

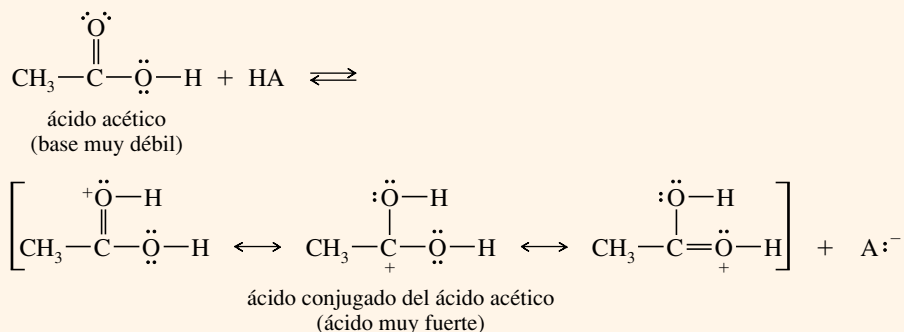
- (a) El etanol puede protonarse en su átomo de oxígeno. Observe que uno de los pares solitarios del oxígeno forma el nuevo enlace O—H.



- (b) El átomo de nitrógeno de la metilamina tiene un par de electrones que pueden enlazarse con un protón.



- (c) El ácido acético tiene electrones no enlazantes en los dos átomos de oxígeno. Cada uno de estos átomos de oxígeno podría protonarse, pero la protonación de oxígeno que forma parte del doble enlace está favorecida porque la protonación de este oxígeno da lugar a un ácido conjugado simétrico y estabilizado por resonancia.



**PROBLEMA 1.16**

El Problema resuelto 1.5(c) muestra la protonación del oxígeno con doble enlace del ácido acético. Escriba el producto obtenido de la protonación en el otro oxígeno ( $\text{—OH}$ ). Explique por qué la protonación del oxígeno con doble enlace está favorecida.

**PROBLEMA 1.17**

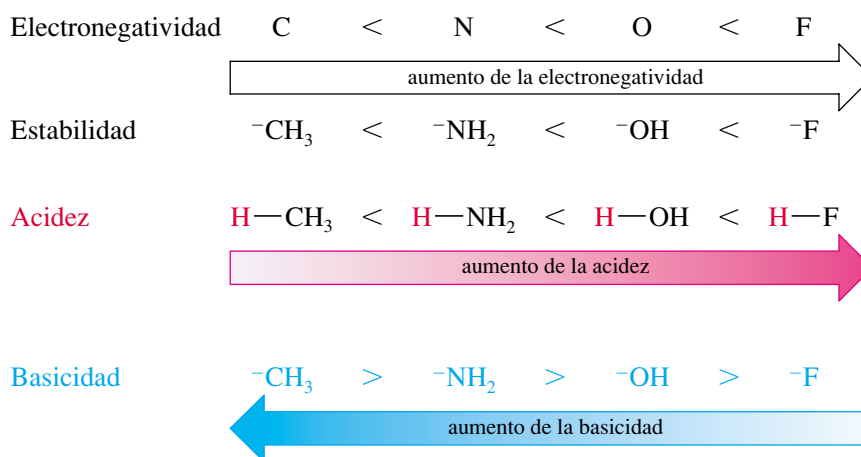
- (a) Ordene por orden decreciente de acidez el etanol, la metilamina y el ácido acético.  
 (b) Ordene por orden decreciente de basicidad el etanol, la metilamina ( $\text{p}K_b = 3.36$ ) y el ión etóxido ( $\text{CH}_3\text{CH}_2\text{O}^-$ ). En cada caso, explique las razones de este orden.

**1.13C Efectos estructurales en la acidez**

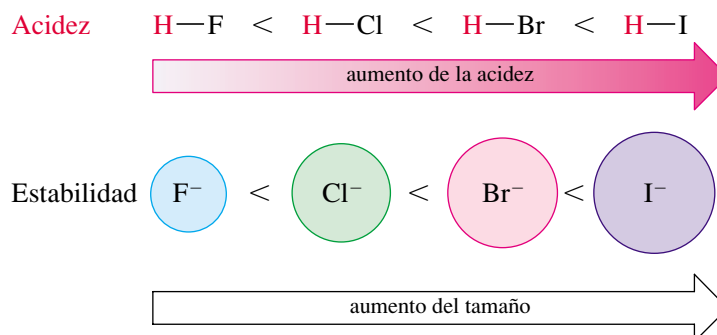
Cuando se observa una estructura, ¿cómo se puede predecir si el compuesto será un ácido fuerte o débil, o bien si no tendrá nada de carácter ácido? Según la teoría de Brønsted-Lowry, un ácido (HA) es un compuesto que ha de contener un átomo de hidrógeno que puede ser cedido como un protón. Un ácido fuerte debe formar una base conjugada estable ( $\text{A}^-$ ) después de perder el protón.

La estabilidad de la base conjugada es una buena guía para conocer la fuerza del ácido. Los aniones más estables tienden a ser bases más débiles y sus ácidos conjugados tienden a ser ácidos más fuertes. Algunos de los factores que afectan a la estabilidad de las bases conjugadas son la electronegatividad, el tamaño y la resonancia.

**Electronegatividad** Cuanto más electronegativo sea un elemento, será capaz de adquirir una carga negativa con más facilidad, lo que dará lugar a una base conjugada más estable y a un ácido fuerte. La electronegatividad aumenta de izquierda a derecha en la tabla periódica.



**Tamaño** La carga negativa de un anión es más estable cuando se distribuye sobre una región del espacio más amplia. Si se considera una columna de la tabla periódica, la acidez aumenta hacia abajo, a medida que el tamaño de los elementos aumenta.



**Estabilización por resonancia** La carga negativa de una base conjugada puede estar deslocalizada entre dos o más átomos, y estabilizada por resonancia. Dependiendo de la electronegatividad que tengan esos átomos y de cómo se comparta esa carga, la deslocalización por resonancia con frecuencia es el efecto dominante que ayuda a la estabilización del anión. Observe las bases conjugadas siguientes:

Base conjugada	Ácido	pK <sub>a</sub>
$\text{CH}_3\text{CH}_2-\ddot{\text{O}}:^-$ ión etóxido	$\text{CH}_3\text{CH}_2-\text{OH}$ etanol	15.9 (ácido débil)
$\left[ \text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\ddot{\text{O}}:^- \longleftrightarrow \text{CH}_3-\overset{\text{:O}:^-}{\parallel}{\text{C}}-\ddot{\text{O}}: \right]$ ión acetato	$\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}$ ácido acético	4.74 (ácido moderado)
$\left[ \text{CH}_3-\overset{\text{O}}{\parallel}{\text{S}}(\ddot{\text{O}})-\ddot{\text{O}}:^- \longleftrightarrow \text{CH}_3-\overset{\text{:O}:^-}{\parallel}{\text{S}}(\ddot{\text{O}})-\ddot{\text{O}}: \longleftrightarrow \text{CH}_3-\overset{\text{O}}{\parallel}{\text{S}}(\ddot{\text{O}})-\ddot{\text{O}}:^- \right]$ ión metanosulfonato	$\text{CH}_3-\overset{\text{O}}{\parallel}{\text{S}}(\text{O})-\text{OH}$ ácido metanosulfónico	-1.2 (ácido fuerte)

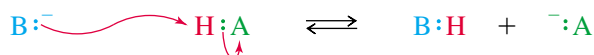
El ión etóxido es el más fuerte de las tres bases anteriores. El etóxido tiene una carga negativa localizada en un átomo de oxígeno; el ión acetato tiene una carga negativa compartida por dos átomos de oxígeno y el ión metanosulfonato tiene una carga negativa extendida sobre tres átomos de oxígeno. Los valores de los pK<sub>a</sub> de los ácidos conjugados de esos aniones muestran que los ácidos son más fuertes si su desprotonación da lugar a bases conjugadas estabilizadas por resonancia.

### PROBLEMA 1.18

Escriba las ecuaciones correspondientes a las reacciones ácido-base siguientes. Señale los ácidos y bases conjugados y justifique, si es el caso, su estabilización por resonancia escribiendo las posibles formas resonantes. Prediga si el equilibrio está desplazado hacia los reactivos o hacia los productos.

- (a)  $\text{CH}_3\text{CH}_2\text{OH} + \text{CH}_3\text{NH}^-$       (b)  $\text{CH}_3\text{CH}_2\text{COOH} + \text{CH}_3\text{NHCH}_3$   
 (c)  $\text{CH}_3\text{OH} + \text{H}_2\text{SO}_4$       (d)  $\text{NaOH} + \text{H}_2\text{S}$   
 (e)  $\text{CH}_3\text{NH}_3^+ + \text{CH}_3\text{O}^-$       (f)  $\text{CH}_3\text{O}^- + \text{CH}_3\text{COOH}$   
 (g)  $\text{CH}_3\text{SO}_3^- + \text{CH}_3\text{COOH}$

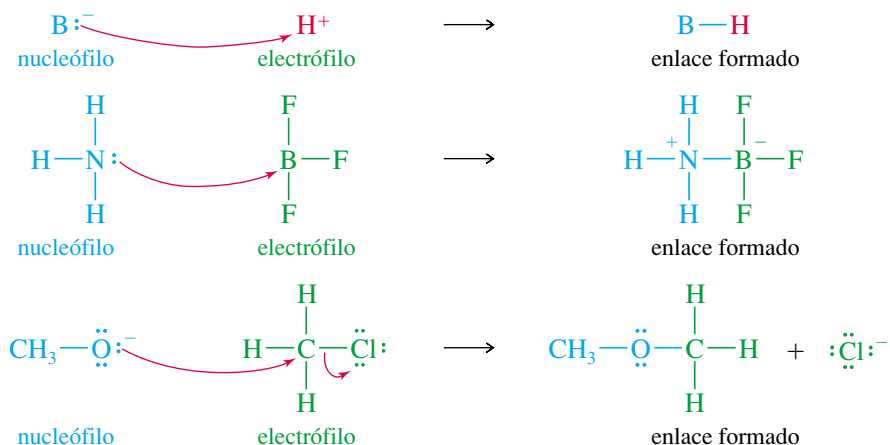
La definición de Brönsted-Lowry de ácidos y bases depende de la transferencia de un protón del ácido a la base. La base utiliza un par de electrones no enlazantes para formar un enlace con el protón. G. N. Lewis pensó que esta clase de reacciones no necesitaba obligatoriamente un protón para tener lugar. Una base podría usar su par solitario de electrones para enlazarse a algún otro átomo deficiente en electrones. En efecto, puede haber reacciones ácido-base desde el punto de vista de los *enlaces* que se forman y rompen, sin necesidad de que se transfiera un protón. La siguiente reacción muestra la transferencia del protón haciendo hincapié en los enlaces que se forman y que se rompen. Los químicos orgánicos utilizan de forma rutinaria flechas curvadas para mostrar el movimiento de los electrones que participan,



Las **bases de Lewis** son especies con electrones no enlazantes que pueden ser cedidos para formar nuevos enlaces. Los **ácidos de Lewis** son especies que pueden aceptar esos pares de electrones para formar nuevos enlaces. Debido a que un ácido de Lewis *acepta* un par de electrones, se le conoce como **electrófilo**, palabra derivada del griego, que significa «amante de electrones». A la base de Lewis se le llama **nucleófilo**, o «amante de los núcleos», ya que cede electrones a un núcleo que tenga un orbital vacío (o prácticamente vacío). En este libro, a veces se usan caracteres coloreados para enfatizar: azul para los nucleófilos, verde para los electrófilos y ocasionalmente rojo para los protones ácidos.

## 1.14 Ácidos y bases de Lewis

Las definiciones ácido-base de Lewis incluyen reacciones que no tienen ninguna relación con los protones. A continuación se muestran algunos ejemplos de reacciones ácido-base de Lewis. Observe que los ácidos y las bases de Brønsted-Lowry también están incluidos dentro de la definición de Lewis, siendo el protón un electrófilo. Las flechas curvadas (rojas) se usan para mostrar el movimiento de los electrones, generalmente desde el nucleófilo al electrófilo.

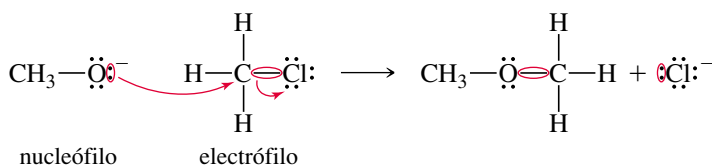


Algunos de los términos asociados con los ácidos y bases poseen significados específicos en química orgánica. Cuando un químico orgánico utiliza el término *base*, normalmente quiere decir «aceptor de protones» (una base de Brønsted-Lowry). De manera similar, el término *ácido* normalmente implica a un protón ácido (un ácido de Brønsted-Lowry). Cuando una reacción ácido-base implica la formación de un enlace con otro elemento (especialmente carbono), un químico orgánico denomina al donador de electrones *nucleófilo* (base de Lewis) y al aceptor de electrones, *electrófilo* (ácido de Lewis).

Las **flechas curvadas** se utilizan para mostrar el movimiento de un par de electrones *desde el donador de electrones al aceptor de electrones*. El movimiento de cada par de electrones implicado en formar o romper enlaces se indica por sus propias flechas separadas, como se muestra en las reacciones anteriores. En este libro, estas flechas curvadas se dibujan siempre en rojo. En la reacción anterior del  $CH_3O^-$  con  $CH_3Cl$ , una flecha curvada muestra el par solitario del oxígeno formando un enlace con el carbono; otra flecha curvada muestra que el par enlazante del  $C-Cl$  se separa del átomo de carbono y se transforma en un par solitario formando el ión  $Cl^-$ .

## SUGERENCIA PARA RESOLVER PROBLEMAS

Utilice una flecha curvada para cada par de electrones que participen en la reacción.



La flecha curvada se usa universalmente para seguir el camino del movimiento de los electrones en las reacciones; en este libro también se ha utilizado (en la Sección 1.9, por ejemplo) para seguir el movimiento de los electrones en las estructuras de resonancia, con objeto de representar el supuesto «flujo electrónico» cuando se pasaba de una estructura de resonancia a otra. Recuerde que los electrones no «fluyen» en las estructuras de resonancia, simplemente están deslocalizados. Este formalismo de las flechas nos ayuda, sin embargo, a comprender la interconversión entre las formas resonantes. Estas flechas curvadas se usan constantemente para seguir el camino de los electrones, tanto en el cambio de reactivos a productos como cuando imaginamos nuevas estructuras resonantes adicionales de un híbrido de resonancia.

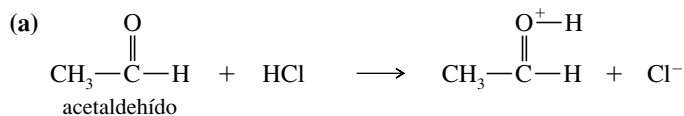
### PROBLEMA 1.19 (parcialmente resuelto)

En las siguientes reacciones ácido-base:

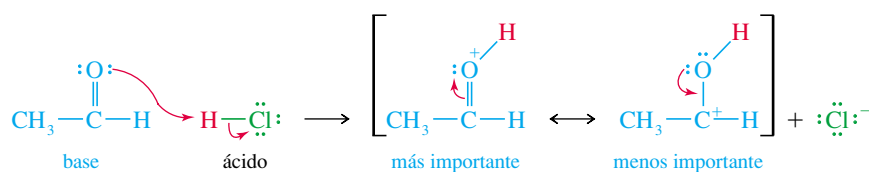
- (1) Determine qué especies actúan como ácidos y cuáles como bases.
- (2) Utilice las flechas curvadas para mostrar el movimiento de los pares de electrones de las reacciones, así como el movimiento imaginario de electrones en los híbridos de resonancia de los productos.



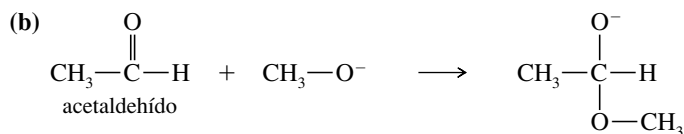
(3) Indique qué reacciones son las más apropiadas para poderlas incluir dentro de las reacciones ácido-base de Brønsted-Lowry.



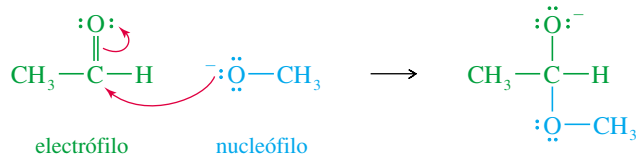
En esta reacción hay transferencia del protón del HCl al grupo C=O del acetaldehído, por tanto, es una reacción ácido-base de Brønsted-Lowry, donde el HCl actúa como ácido (donador de protones) y el acetaldehído actúa como base (aceptor de protones). Antes de dibujar una flecha curvada, recuerde que las flechas deben mostrar el movimiento de los electrones *desde* el donador del par de electrones (la base) *hasta* el aceptor del par de electrones (el ácido). Una flecha debe ir *desde* los electrones no enlazantes del acetaldehído *hasta* el átomo de hidrógeno del HCl y el enlace del ácido clorhídrico se ha de romper, con la formación del ión cloruro que ha captado los electrones del enlace H—Cl. Dibujar las flechas es fácil después de haber representado correctamente estructuras de Lewis de todos los reactivos y productos.



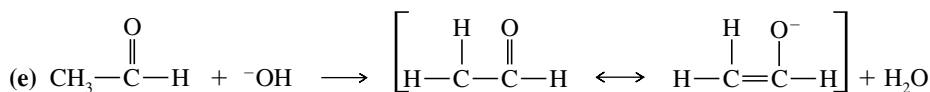
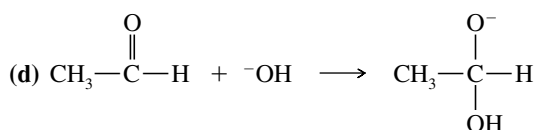
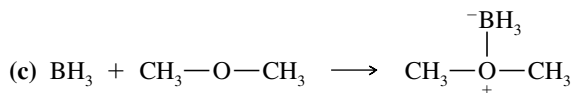
Las formas de resonancia del producto muestran que un par de electrones puede moverse entre el átomo de oxígeno y el enlace pi del C=O. La carga positiva está deslocalizada sobre los átomos de carbono y de oxígeno, con la mayor parte de la carga positiva sobre el oxígeno, ya que todos los octetos están completos en esa estructura de resonancia.



En este caso, ningún protón se ha transferido, por lo que no es una reacción ácido-base de Brønsted-Lowry. En su lugar, se ha formado un enlace entre el átomo de carbono del grupo C=O y el átomo de oxígeno del grupo CH<sub>3</sub>—O<sup>−</sup>. Dibujar las estructuras de Lewis ayuda a ver que el grupo CH<sub>3</sub>—O<sup>−</sup> (el nucleófilo en esta reacción) cede los electrones para formar el nuevo enlace con el acetaldehído (el electrófilo). Este resultado concuerda con la intuición de que un ión cargado negativamente es probablemente rico en electrones y por tanto un donador de electrones.



Observe que el acetaldehído actúa como nucleófilo (base) en (a) y como electrófilo en (b). Como la mayoría de los compuestos orgánicos, el acetaldehído puede ser tanto un ácido como una base. Actúa como una base si se le añade un ácido lo suficientemente fuerte para que ceda un par de electrones o capte un protón.



## SUGERENCIA PARA RESOLVER PROBLEMAS

Las flechas curvadas se utilizan en los mecanismos para mostrar el *flujo de electrones* y no el movimiento de los átomos. Estas flechas curvadas se usarán constantemente a lo largo de este curso.

## Glosario del Capítulo 1

Cada capítulo finaliza con un glosario que recoge los términos nuevos más importantes del capítulo. Estos glosarios son más que un diccionario en el que se buscan términos desconocidos conforme se los vaya encontrando (el índice sirve para este propósito). El glosario es una de las herramientas para revisar el capítulo, se puede leer cuidadosamente para saber si se entienden y se recuerdan todos los términos químicos mencionados. Cualquier concepto que no resulte familiar debería ser revisado volviendo a la página que aparece numerada en el mismo.

**Ácido conjugado** El ácido que resulta de la protonación de una base. (p. 23)

**Ácido de Lewis, base de Lewis.** Véase ácidos y bases.

**Ácidos y bases** (pp. 21-31)

(definiciones de Arrhenius)

(definiciones de Brønsted-Lowry)

(definiciones de Lewis)

**Ácido:** se disocia en agua para dar  $\text{H}_3\text{O}^+$ .

**Base:** se disocia en agua para dar  $\text{OH}^-$ .

**Ácido:** donador de protones.

**Base:** aceptor de protones.

**Ácido:** aceptor de un par de electrones (electrófilo).

**Base:** donador de un par de electrones (nucleófilo).

**Base conjugada** La base que resulta de la pérdida de un protón de un ácido. (p. 23)

**Cargas formales** Método para hacer un seguimiento de las cargas, el cual permite mostrar qué carga habría en una determinada estructura de Lewis. (p. 11)

**Densidad electrónica** Probabilidad relativa de encontrar un electrón en una cierta región del espacio. (p. 3)

**Electrófilo** Aceptor de un par de electrones. (p. 29)

**Electronegatividad** Medida de la capacidad de un elemento para atraer electrones. Los elementos con electronegatividades más altas atraen a los electrones con más fuerza. (p. 10)

**Electrones de valencia** Electrones que se encuentran en la capa externa más alejada del núcleo. (p. 6)

**Electrones no enlazantes** Electrones de valencia que no se utilizan en el enlace. A un par de electrones no enlazantes con frecuencia se le denomina **par solitario**. (p. 7)

**Enlace covalente** Enlace que se forma por la compartición de electrones en la región que hay entre dos núcleos. (p. 7)

**Enlace sencillo:** enlace covalente en el que se comparte un par de electrones. (p. 8)

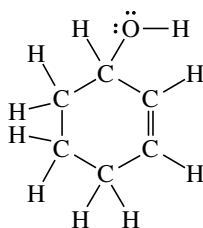
**Enlace doble:** enlace covalente en el que se comparte dos pares de electrones. (p. 8)

**Enlace triple:** enlace covalente en el que se comparte tres pares de electrones. (p. 8)

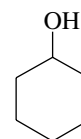
**Enlace covalente polar** Enlace covalente en el que los electrones se comparten de forma desigual. Cuando los electrones están igualmente compartidos se llama **enlace covalente no polar**. (p. 9)

**Enlace iónico** Enlace que se produce por la atracción de iones que tienen carga opuesta. El enlace iónico normalmente da lugar a la formación de una gran estructura cristalina en tres dimensiones. (p. 7)

**Estructura de Lewis** Fórmula estructural que muestra todos los electrones de valencia, con los enlaces simbolizados por líneas (—) o por pares de puntos, y los electrones no enlazantes simbolizados por puntos. (p. 7)



estructura de Lewis del 2-ciclohexenol



2-ciclohexenol  
fórmula lineoangular equivalente

**Flechas curvadas** El dibujar flechas curvadas es un método que se utiliza para seguir el camino de los electrones cuando se mueven desde el nucleófilo al electrófilo (o dentro de una molécula) durante el transcurso de una reacción. (p. 30)

**Fórmula empírica** Relación numérica de los átomos en un compuesto. (p. 20). Véase también **fórmula molecular**.

**Fórmula lineoangular (estructura esquelética o de barras)** Fórmula estructural con enlaces representados por líneas; los átomos de carbono son los puntos de encuentro entre dos líneas o el final de la línea cuando está en el extremo de la cadena. Los átomos de nitrógeno, de oxígeno y los halógenos se representan, pero los átomos de hidrógeno no. Se supone que cada átomo de carbono tiene los hidrógenos suficientes para que en total tenga cuatro enlaces. (p. 19)

**Fórmula molecular** Número de átomos de cada elemento que forman parte de una molécula de un compuesto. La **fórmula empírica** simplemente da la relación de los átomos de los diferentes elementos. Por ejemplo, la fórmula molecular de la glucosa es  $C_6H_{12}O_6$ ; su fórmula empírica es  $CH_2O$ . Ni la fórmula empírica ni la fórmula molecular dan información estructural. (p. 4)

**Fórmulas estructurales** Una **fórmula estructural completa** (tal como una estructura de Lewis) muestra todos los átomos y enlaces en la molécula. Una **fórmula estructural condensada** muestra cada átomo central y los átomos con los que está enlazado. Una **fórmula lineoangular** supone que hay un átomo de carbono donde dos líneas se encuentren, o donde la línea comience o termine. Véanse los ejemplos de la Sección 1.10. (p. 17)

**Híbrido de resonancia** Molécula o ión para el cual se pueden representar dos o más estructuras de Lewis válidas, diferenciándose solamente en la posición de los electrones de valencia. Estas estructuras de Lewis se conocen como **formas de resonancia** o **estructuras de resonancia**. Las formas de resonancia individuales no existen, pero se puede estimar sus energías relativas. A las estructuras más importantes (de energía más baja) se las conoce como **contribuyentes mayores**, y a las estructuras menos importantes (energía más alta), como **contribuyentes menores**. Cuando una carga se reparte entre dos o más átomos por resonancia, se dice que está **deslocalizada** y que la molécula está **estabilizada por resonancia**. (pp. 13-16)

**Isótopos** Átomos con el mismo número de protones pero diferente número de neutrones. Átomos del mismo elemento pero con diferentes masas atómicas. (p. 3)

**Mapa de potencial electrostático (MPE)** Representación molecular calculada por computador que utiliza colores para mostrar la distribución de carga en una molécula. En la mayoría de los casos, el MPE utiliza el color rojo para indicar las regiones ricas en electrones (potencial electrostático más negativo) y azul para indicar las regiones pobres en electrones (potencial electrostático más positivo). Los colores intermedios naranja, amarillo y verde indican regiones con potenciales electrostáticos intermedios. (p. 10)

**Momento dipolar ( $\mu$ )** Medida de la polaridad de un enlace (o una molécula), proporcional al producto de la separación de cargas por la longitud de enlace. (p. 10)

**Nodo** Región de un orbital con densidad electrónica cero. (p. 4)

**Nucleófilo** Donador de par de electrones (base de Lewis). (p. 29)

**Orbital** Estado de energía permitida para un electrón que rodea a un núcleo; función de probabilidad que define la distribución de la densidad electrónica en el espacio. El *principio de exclusión de Pauli* afirma que un orbital sólo puede ser ocupado por dos electrones, como máximo, si los espines de éstos están apareados. (p. 3)

**Orbitales degenerados** Orbitales con energías idénticas. (p. 4)

**Par solitario** Par de electrones no enlazantes. (p. 7)

**pH** Medida de la acidez de una solución, definido como el logaritmo (en base 10), cambiado de signo, de la concentración de  $H_3O^+$ .  $pH = -\log_{10}[H_3O^+]$ . (p. 22)

**Plano nodal** Región plana (plano) del espacio con densidad electrónica cero. (p. 4)

**Química orgánica** Definición nueva: química de los compuestos de carbono. Definición antigua: estudio de los compuestos derivados de los organismos vivos y sus productos naturales. (p. 1)

**Regla de Hund** Cuando hay dos orbitales o más con la misma energía (orbitales degenerados) vacíos, la configuración de energía más baja se consigue colocando los electrones en orbitales diferentes (con espines paralelos), mejor que colocándolos apareados en el mismo orbital. (p. 6)

**Regla del octeto** Los átomos generalmente se enlazan para que sus capas de valencia se completen con electrones (configuración de gas noble). Para los elementos de la segunda fila de la tabla periódica, esta configuración tiene ocho electrones de valencia. (p. 6)

**Valencia** Número de enlaces que normalmente forma un átomo. (p. 9)

**Vitalismo** Creencia en que la síntesis de compuestos orgánicos requiere la presencia de una «fuerza vital». (p. 1)

### Pautas esenciales para resolver los problemas del Capítulo 1

1. Escribir e interpretar las fórmulas estructurales de Lewis, condensadas y lineoangulares. Indicar qué átomos tienen cargas formales.
2. Escribir formas de resonancia y usarlas para predecir la estabilidad.
3. Calcular fórmulas empíricas y moleculares de composiciones elementales.
4. Predecir la acidez y la basicidad relativa basada en la estructura, en el enlace y en la resonancia de los pares ácido-base conjugados.
5. Calcular, usar e interpretar los valores de  $K_a$  y  $pK_a$ .
6. Identificar nucleófilos (bases de Lewis) y electrófilos (ácidos de Lewis) y escribir ecuaciones de reacciones ácido-base de Lewis utilizando flechas curvadas para mostrar el flujo de los electrones.

## Problemas

Es fácil engañarse a uno mismo pensando que se entiende la química orgánica cuando realmente no se entiende. Según se van leyendo a lo largo de este libro, todos los conceptos y las ideas pueden tener sentido, pero todavía no se ha aprendido a combinar y a usar esos conceptos e ideas. Un examen es un trance duro para darse cuenta de que realmente no se han entendido los contenidos.

La mejor forma de aprender química orgánica es aplicarla. Por supuesto se necesita leer y releer todo el material del capítulo, pero este nivel de entendimiento es justamente el comienzo. Se proponen problemas para poder trabajar con las ideas, aplicándolas a nuevos compuestos y reacciones que no se han visto con anterioridad. Al resolver problemas, uno se ve obligado a utilizar los conceptos y a entender lo que antes no se había comprendido, también se aumenta el nivel de autoestima y de habilidad para realizar los exámenes.

En cada capítulo se incluyen varias clases de problemas. Hay problemas dentro de los capítulos, que se introducen como ejemplos y explican cómo se han de resolver. Se ha de realizar ese tipo de problemas según se vaya leyendo el capítulo para asegurarse de que se han entendido los conceptos. Las soluciones de muchos de estos problemas se encuentran al final de libro. Los Problemas del final de cada capítulo proporcionan una experiencia adicional en el uso de los conceptos y obligan a pensar con detenimiento sobre las ideas expuestas en el texto. Para algunos de estos problemas se incluyen soluciones breves al final del libro, sin embargo, se pueden encontrar soluciones más detalladas de los mismos en el *Manual de Soluciones*.

Estudiar química orgánica sin resolver problemas es como lanzarse al aire sin paracaídas. Al principio parece divertido, pero después puede resultar duro para aquellos que carezcan de preparación.

**1.20** Defina y ponga un ejemplo para cada término:

- |                                    |                            |                               |
|------------------------------------|----------------------------|-------------------------------|
| (a) isótopos                       | (b) orbital                | (c) nodo                      |
| (d) orbitales degenerados          | (e) electrones de valencia | (f) enlace iónico             |
| (g) enlace covalente               | (h) estructura de Lewis    | (i) electrones no enlazantes  |
| (j) enlace sencillo                | (k) enlace doble           | (l) enlace triple             |
| (m) enlace polar                   | (n) cargas formales        | (o) formas de resonancia      |
| (p) fórmula molecular              | (q) fórmula empírica       | (r) ácido y base de Arrhenius |
| (s) ácido y base de Brønsted-Lowry | (t) ácido y base de Lewis  | (u) electrófilo               |
| (v) nucleófilo                     |                            |                               |

**1.21** Nombre el elemento que corresponda a cada configuración electrónica.

- (a)  $1s^2 2s^2 2p^2$       (b)  $1s^2 2s^2 2p^4$       (c)  $1s^2 2s^2 2p^6 3s^2 3p^3$       (d)  $1s^2 2s^2 2p^6 3s^2 3p^5$

**1.22** Hay una pequeña sección de la tabla periódica que se debe conocer en química orgánica. Escriba de memoria esta parte, realizando los siguientes pasos:

- (a) Haga una lista, de memoria, de los elementos de las dos primeras filas de la tabla periódica, junto con su número de electrones de valencia.  
 (b) Use esta lista para construir las dos primeras filas de la tabla periódica.  
 (c) Los compuestos orgánicos a veces contienen azufre, fósforo, cloro, bromo y yodo. Añada estos elementos a la tabla periódica.

**1.23** Para cada compuesto, diga si el enlace es covalente, iónico, o intermedio entre covalente e iónico.

- (a) NaCl      (b) NaOH      (c)  $\text{CH}_3\text{Li}$       (d)  $\text{CH}_2\text{Cl}_2$       (e)  $\text{NaOCH}_3$       (f)  $\text{HCO}_2\text{Na}$       (g)  $\text{CF}_4$

**1.24** (a) El  $\text{PCl}_3$  y el  $\text{PCl}_5$  son compuestos estables. Escriba la estructura de Lewis para los dos compuestos.

- (b) El  $\text{NCl}_3$  es un compuesto conocido, pero todos los intentos de sintetizar el  $\text{NCl}_5$  han fracasado. Escriba las estructuras de Lewis para el  $\text{NCl}_3$  y una hipotética para el  $\text{NCl}_5$ , y explique por qué el  $\text{NCl}_5$  es una estructura improbable.

**1.25** Escriba una estructura de Lewis para cada una de las especies.

- (a)  $\text{N}_2\text{H}_4$       (b)  $\text{N}_2\text{H}_2$       (c)  $(\text{CH}_3)_4\text{NCl}$       (d)  $\text{CH}_3\text{CN}$       (e)  $\text{CH}_3\text{CHO}$       (f)  $\text{CH}_3\text{S(O)CH}_3$   
 (g)  $\text{H}_2\text{SO}_4$       (h)  $\text{CH}_3\text{NCO}$       (i)  $\text{CH}_3\text{OSO}_2\text{OCH}_3$       (j)  $\text{CH}_3\text{C(NH)CH}_3$       (k)  $(\text{CH}_3)_3\text{CNO}$

**1.26** Escriba una estructura de Lewis para cada compuesto. Incluya todos los pares de electrones no enlazantes.

- (a)  $\text{CH}_3\text{CHCHCH}_2\text{CHCHCOOH}$       (b)  $\text{NCCH}_2\text{COCH}_2\text{CHO}$   
 (c)  $\text{CH}_2\text{CHCH(OH)CH}_2\text{CO}_2\text{H}$       (d)  $\text{CH}_3\text{CH(CH}_3\text{)CH}_2\text{C(CH}_2\text{CH}_3\text{)}_2\text{CHO}$

**1.27** Escriba la fórmula lineoangular de todos los compuestos del Problema 1.26.

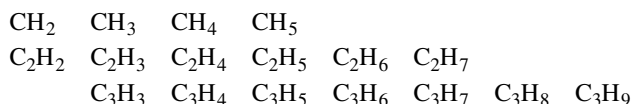
**1.28** Escriba las estructuras de Lewis para:

- (a) dos compuestos de fórmula  $\text{C}_4\text{H}_{10}$       (b) dos compuestos de fórmula  $\text{C}_2\text{H}_7\text{N}$   
 (c) dos compuestos de fórmula  $\text{C}_3\text{H}_8\text{O}_2$       (d) dos compuestos de fórmula  $\text{C}_2\text{H}_4\text{O}$

**1.29** Represente una fórmula estructural completa y una fórmula estructural condensada para:

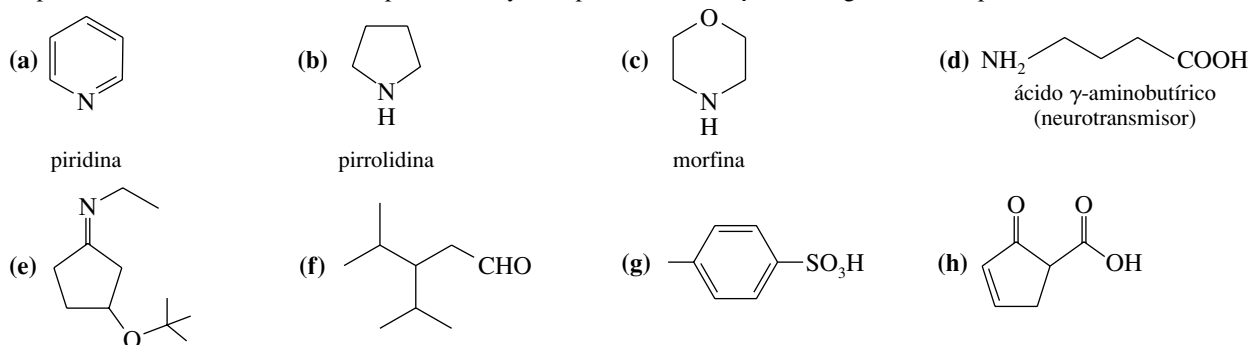
- (a) tres compuestos de fórmula  $\text{C}_3\text{H}_8\text{O}$       (b) cinco compuestos de fórmula  $\text{C}_3\text{H}_6\text{O}$

**1.30** Alguna de las siguientes fórmulas moleculares corresponde a compuestos estables. Represente, cuando sea posible, una estructura estable para cada fórmula.



Proponga una regla general que dé el número de átomos de hidrógeno en los hidrocarburos estables.

1.31 Represente estructuras de Lewis completas, incluyendo pares solitarios, para los siguientes compuestos:



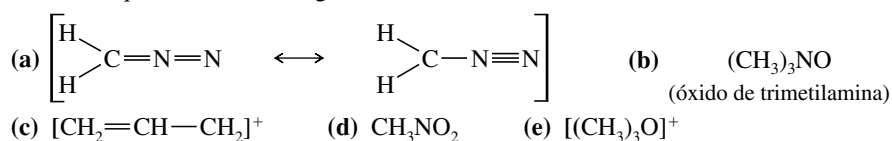
1.32 Escriba la fórmula molecular de todos los compuestos del Problema 1.31.

1.33 Un compuesto X, aislado de la lanolina (grasa de la lana de oveja), tiene un fuerte aroma a calcetines sucios sudados. Un análisis cuidadoso mostró que el compuesto X contenía un 62.0% de carbono y un 10.4% de hidrógeno. No se encontró nitrógeno ni halógenos.

- (a) Escriba la fórmula empírica del compuesto X.  
 (b) La determinación del peso molecular mostró que el compuesto X tenía un peso molecular aproximadamente igual a 117; encuentre la fórmula molecular del compuesto X.  
 (c) Hay muchas estructuras posibles que tienen esa fórmula molecular. Represente las fórmulas estructurales completas de cuatro de ellas.

1.34 Para cada una de las siguientes estructuras:

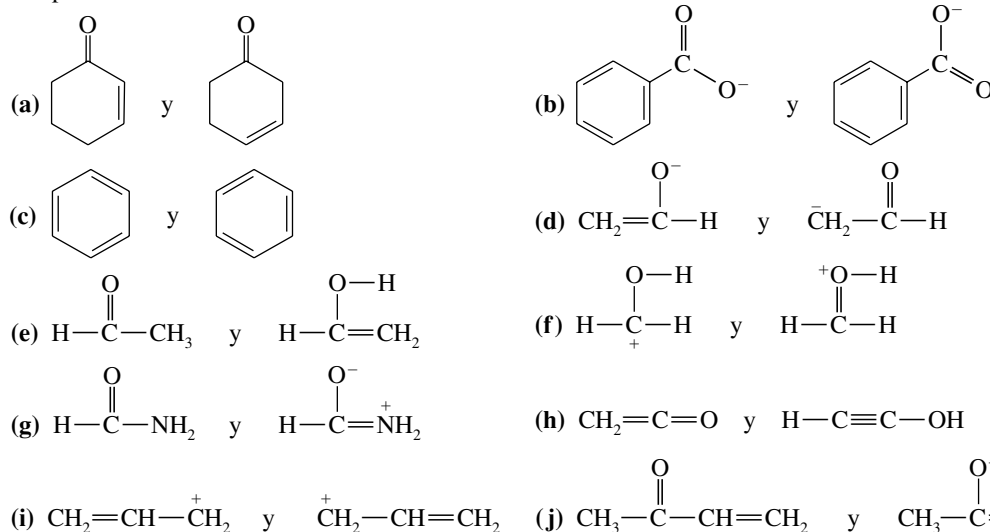
- (1) Represente una estructura de Lewis, poniendo también los electrones no enlazantes.  
 (2) Calcule la carga formal de todos los átomos excepto del hidrógeno. Todos son eléctricamente neutros excepto aquellos en los que se indica su carga.



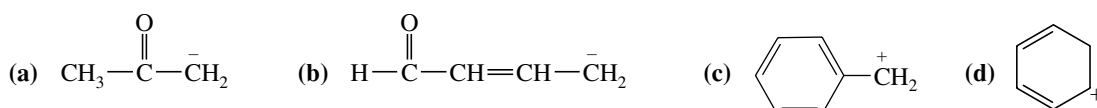
1.35 (1) Teniendo en cuenta la electronegatividad, establezca la dirección de los momentos dipolares de los siguientes enlaces.  
 (2) En cada caso, prediga si el momento dipolar es relativamente grande o pequeño.

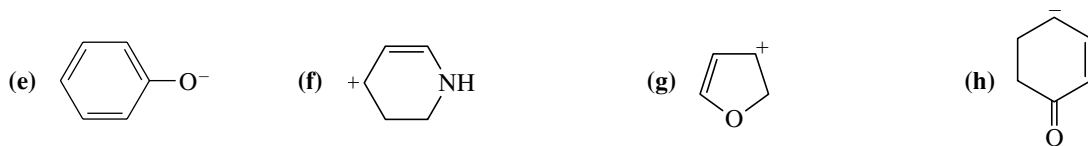
- (a)  $\text{C}-\text{Cl}$  (b)  $\text{C}-\text{H}$  (c)  $\text{C}-\text{Li}$  (d)  $\text{C}-\text{N}$  (e)  $\text{C}-\text{O}$   
 (f)  $\text{C}-\text{B}$  (g)  $\text{C}-\text{Mg}$  (h)  $\text{N}-\text{H}$  (i)  $\text{O}-\text{H}$  (j)  $\text{C}-\text{Br}$

1.36 Determine si los siguientes pares de estructuras son diferentes compuestos o solamente formas de resonancia del mismo compuesto.



1.37 Represente las formas de resonancia importantes para mostrar la deslocalización de cargas en los iones siguientes:





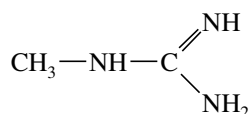
1.38

- (a) Represente las formas de resonancia para el  $\text{SO}_2$  (conectividad  $\text{O}-\text{S}-\text{O}$ ).  
 (b) Represente las formas de resonancia para el ozono (conectividad  $\text{O}-\text{O}-\text{O}$ ).  
 (c) El dióxido de azufre tiene una forma de resonancia más que el ozono, explique por qué esa estructura no es posible para el ozono.

\*1.39

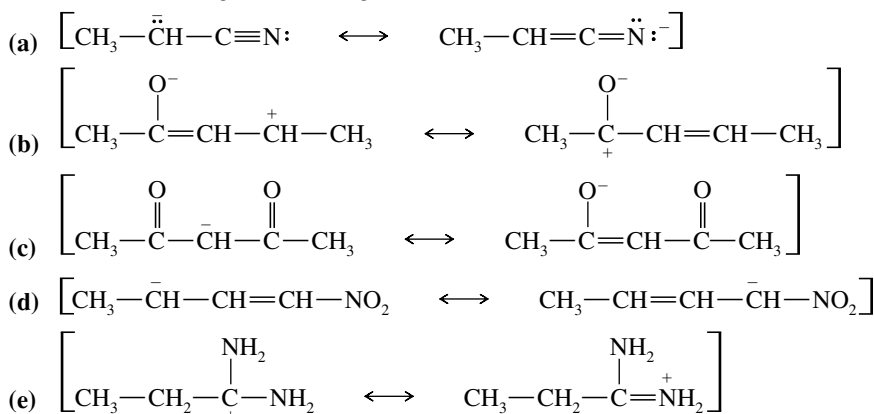
El compuesto siguiente puede protonarse en cualquiera de los átomos de nitrógeno, no obstante, uno de esos nitrógenos es mucho más básico que los otros.

- (a) Represente las formas de resonancia importantes de los productos de protonación de cada uno de los tres átomos de nitrógeno.  
 (b) Determine qué átomo de nitrógeno es el más básico.



1.40

En los siguientes apartados de formas de resonancia, señale los contribuyentes mayor y menor, y diga qué estructuras tienen la misma energía. Si falta alguna forma de resonancia, añádala.



1.41

Para cada par de iones, determine cuál es más estable. Use formas de resonancia para explicar las respuestas.

- (a)  $\text{CH}_3-\overset{+}{\text{C}}\text{H}-\text{CH}_3$  o  $\text{CH}_3-\overset{+}{\text{C}}\text{H}-\text{OCH}_3$   
 (b)  $\text{CH}_2=\text{CH}-\overset{+}{\text{C}}\text{H}-\text{CH}_3$  o  $\text{CH}_2=\text{CH}-\text{CH}_2-\overset{+}{\text{C}}\text{H}_2$   
 (c)  $\overset{-}{\text{C}}\text{H}_2-\text{CH}_3$  o  $\overset{-}{\text{C}}\text{H}_2-\text{C}\equiv\text{N}:$



1.42

Ordene las siguientes especies por orden creciente de acidez, explicando las razones de este ordenamiento.



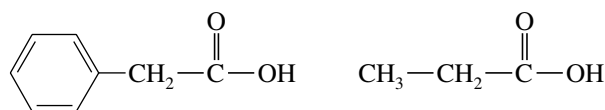
1.43

Ordene las siguientes especies por orden creciente de basicidad, explicando las razones de este ordenamiento.



1.44

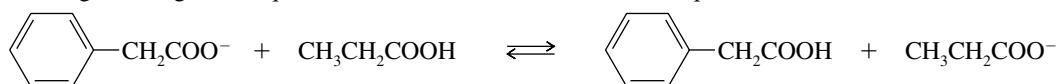
La  $K_a$  del ácido fenilacético es  $5.2 \times 10^{-5}$  y el  $pK_a$  del ácido propiónico es 4.87.

ácido fenilacético,  $K_a = 5.2 \times 10^{-5}$ ácido propiónico,  $pK_a = 4.87$ 

- (a) Calcule el  $pK_a$  del ácido fenilacético y la  $K_a$  del ácido propiónico.

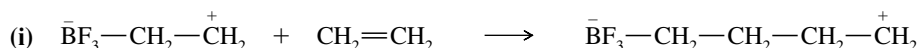
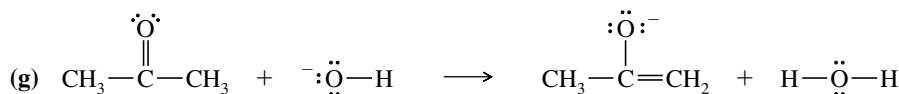
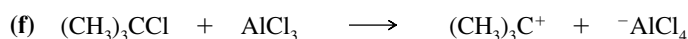
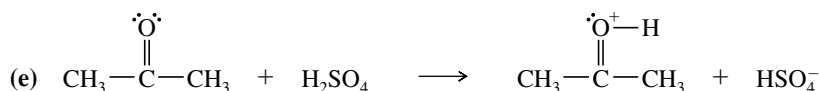
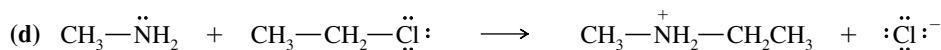
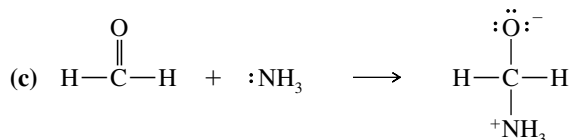
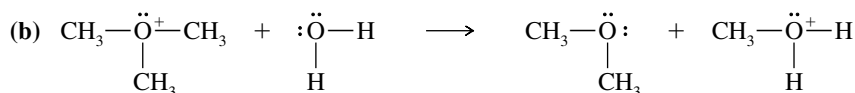
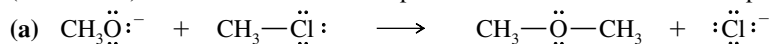
(b) ¿Cuál de los dos ácidos es el más fuerte? Calcule cuánto más fuerte es uno que otro.

(c) Prediga si el siguiente equilibrio favorecerá a los reactivos o a los productos.



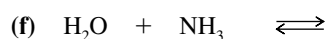
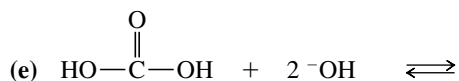
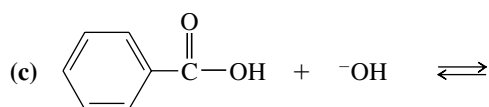
## 1.45

En las siguientes reacciones ácido-base clasifique los reactivos como ácidos de Lewis (electrófilos) o bases de Lewis (nucleófilos). Utilice flechas curvadas para indicar el movimiento de los pares de electrones en las reacciones.



## 1.46

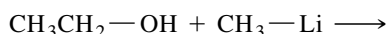
Prediga los productos de las siguientes reacciones ácido-base:



## \*1.47

El metilítio ( $\text{CH}_3\text{Li}$ ) a menudo se usa como base en reacciones orgánicas.

(a) Prediga los productos de la siguiente reacción ácido-base:



(b) ¿Cuál es el ácido conjugado del  $\text{CH}_3\text{Li}$ ? ¿Qué es el  $\text{CH}_3\text{Li}$ ?, ¿una base fuerte o débil?

## \*1.48

En 1984, Edward A. Doisy de la Universidad de Washington extrajo 1 360 kg de ovarios de cerda para aislar unos pocos miligramos de estradiol puro, una potente hormona femenina. Doisy quemó 5.00 mg de esa preciada muestra en oxígeno y encontró que se obtenían 14.54 mg de  $\text{CO}_2$  y 3.97 mg de  $\text{H}_2\text{O}$ .

(a) Determine la fórmula empírica del estradiol.

(b) La masa molecular del estradiol se determinó posteriormente y se encontró que era de 272. Determine la fórmula molecular del estradiol.